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(54) LIQUID COMPOSITION, INK SET, METHOD AND DEVICE FOR FORMING IMAGE USING THEM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain excellent fixability and improve character quality by using a liquid composition to be used together with an ink for forming images, which is prepared by adding a metal coordination compound in a liquid medium.

SOLUTION: For forming images, a liquid composition is used together with an ink. The liquid composition contains a metal coordination compound surrounded by an electron donating body (ligand) having an ability in which a certain type of metal ion bonds to a metal ion by coordinate bonding in addition to a liquid medium. For the ligand which forms the metal coordination compound, a ligand having two or more ligands is used. The metal coordination compound included in the liquid composition and a dye having at least anionic group as a coloring material included in the ink are mixed on a recording medium such as a recording paper. A central metal in the metal coordination compound reacts on the coloring material in the ink, and the coloring material comes to be eluted. Thus, as the dye is eluted, many of dye compounds fix on the surface of the recording medium such as the recording paper.

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## CLAIMS

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[Claim(s)]

[Claim 1] The liquid constituent which is a liquid constituent used with the ink for forming a picture, and is characterized by making a metal coordination compound contain in a liquid medium.

[Claim 2] The liquid constituent according to claim 1 with which the ligand which constitutes the aforementioned metal coordination compound has the two or more coordination numbers.

[Claim 3] The liquid constituent according to claim 1 with which the ligand which constitutes the aforementioned metal coordination compound has the three or more coordination numbers.

[Claim 4] The liquid constituent according to claim 2 or 3 the aforementioned ligand is [ constituent ] in any which are chosen from a glycine, ethylenediamine, a propylenediamine, a lactic acid, iminodiacetate, a diethylenetriamine, a dihydroxyethyl glycine, hydroxyethyl iminodiacetate, nitrilotriacetic acid, ethylenediaminetetraacetic acid, hydroxyethyl ethylenediaminetetraacetic acid, a diethylenetriamine pentaacetic acid, and triethylenetetramine 6 acetic acid.

[Claim 5] The liquid constituent according to claim 1 the metal ion which constitutes the aforementioned metal coordination compound is [ constituent ] in any of aluminum ion, nickel ion, a copper ion, barium ion, calcium ion, iron ion, or chromium ion.

[Claim 6] Furthermore, the liquid constituent according to claim 1 with which number average molecular weight contains 1,000 or more high molecular compounds.

[Claim 7] The liquid constituent according to claim 1 which contains the aforementioned metal coordination compound in 0.05 – 8.0% of the weight of the range.

[Claim 8] The liquid constituent according to claim 1 which contains water and the water-soluble organic solvent as the aforementioned solvent object.

[Claim 9] The liquid constituent according to claim 6 which contains the aforementioned high molecular compound in 0.05 – 20% of the weight of the range.

[Claim 10] The ink set characterized by combining a liquid constituent given in any of claims 1–9 they are, yellow, a Magenta, cyanogen and black, red, blue, and at least one ink of green.

[Claim 11] The ink set characterized by combining a liquid constituent given in any of claims 1–9 they are, and the ink of three colors of yellow, a Magenta, and cyanogen.

[Claim 12] The ink set characterized by combining a liquid constituent given in any of claims 1–9 they are, and the ink of four colors of yellow, a Magenta, cyanogen, and black.

[Claim 13] The ink set given in any of claims 10–12 they are with which ink contains an anionic compound.

[Claim 14] The ink set given in any of claims 10–12 they are with which ink contains the water soluble dye which has an anionic machine.

[Claim 15] An ink set given in any of the claims 10–12 which separated and contained the aforementioned liquid constituent and the aforementioned ink they are.

[Claim 16] The image formation method characterized by including the process (B) which gives the ink which contains an anionic compound for a liquid constituent given in any of claims 1–9 they are at least with the process (A) of a record medium made to adhere to an image formation field at least to the aforementioned record medium with an ink-jet method.

[Claim 17] The image formation method according to claim 16 that the aforementioned ink-jet method is an on-demand type ink-jet method.

[Claim 18] The image formation method according to claim 16 of making the aforementioned liquid constituent adhering to a record medium with an ink-jet method.

[Claim 19] The image formation method given in any of claims 16-18 they are that the aforementioned ink-jet method is an ink-jet method on which heat energy is made to act.

[Claim 20] The image formation method according to claim 16 of performing a process (A) in advance of a process (B).

[Claim 21] The image formation method according to claim 16 of performing a process (A) after a process (B).

[Claim 22] Image formation equipment characterized by having an ink set and an ink-jet means given in any of claims 10-15 they are.

[Claim 23] Image formation equipment characterized by having the first record unit which has the stowage and regurgitation means of a liquid constituent given in any of claims 1-9 they are, and the second record unit which has the stowage and regurgitation means of ink of containing an anionic compound at least.

[Claim 24] Image formation equipment according to claim 23 whose aforementioned regurgitation means is an ink-jet means.

[Claim 25] Image formation equipment according to claim 22 or 24 which is a means by which the aforementioned ink-jet means makes heat energy act, and forms an ink drop.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] about the technology of reducing the so-called color bleeding (phenomenon) produced when forming a color picture in a regular paper, and acquiring the existing ink picture which is water resistance, this invention is divided and relates to the image formation method and image formation equipment using the liquid constituent applied in the image formation using the ink-jet method, the ink set which combined ink with this, and these

[0002]

[Description of the Prior Art] The ink-jet record method makes an ink globule fly, and records by making ink adhere on record media, such as paper. According to the ink-jet record method of a method of making a drop breathing out by giving heat energy to ink, using an electric thermal-conversion object as a regurgitation energy supply means currently especially indicated in JP,61-59912,B and JP,61-59914,B, and generating a foam, high-density multi-orifice-ization of a recording head can be realized easily, and high-speed record of high resolution and a quality picture is attained.

[0003] However, the ink used for the conventional ink-jet record Since what made water the principal component and contained water-soluble high boilers, such as a glycol, for the purpose, such as dryness prevention and blinding prevention, in this is common, When recording using such ink, using a regular paper as a record medium, the problem of the uneven picture presumed not to obtain the fixing nature of sufficient picture or to be based on the uneven distribution of the loading material in a record-medium front face or a sizing compound occurring had arisen. Moreover, in order that the ink of two or more colors might pile up one after another before fixing to each color ink completely in the paper which is a record medium when it is going to obtain especially a color picture, in the unique boundary portion of a picture, there was also a problem that a color did not spread or the picture which should be mixed unevenly (this phenomenon is hereafter called bleeding), and should be satisfied was not acquired.

[0004] On the other hand, as a means which raises the fixing nature of a picture, adding the compound which raises the permeability of a surfactant etc. into ink is indicated by JP,55-65269,A. Moreover, using for JP,55-66976,A the ink which made the volatile solvent the subject is indicated. however, by the former method, as a result of the permeability to record Kaminaka of ink increasing, in order that the recording paper may be deep and color material may also carry out until osmosis with the ink of what can be raised to some extent about fixing nature and bleeding-proof nature, un-arranging [ of picture concentration and saturation falling ] occurs In addition, as a result of also generating the breadth to the longitudinal direction of ink, problems, such as a fall of the sharpness of the edge of a picture and a fall of a definition, are also generated simultaneously. In addition, the blinding by evaporation of the solvent in the nozzle section of a recording head to the former which was described above on the other hand in the case of the latter is easy to generate and is not desirable inconvenient.

[0005] Furthermore, the method of making the liquid constituent which has the function in which a formation picture becomes good in order to improve the various troubles mentioned above

adhere on a record medium in advance of injection of ink is indicated. For example, after making the liquid constituent which the organic compound which has two or more cation nature machines per molecule contained adhere on a record medium in advance of injection of ink, the method of recording in the ink which the anionic color contained is indicated by JP,63-299971,A.

[0006] Moreover, the method of injecting the liquid constituent containing basic polymer in advance of record of ink is indicated by JP,63-60783,A and JP,64-63185,A. however, the above — in order that any method might use the polymer which has a cation nature machine, there was a trouble of reducing the lightfastness of a color remarkably

[0007] On the other hand, in advance of grant of the ink to a record medium, the compound formed of the ionic bond between polyvalent metallic salt, i.e., various metal ions, and anions, such as a halogenated compound and an organic acid, is beforehand given on the record medium, and the method of forming a picture in ink after that is indicated by JP,63-299970,A and JP,5-202328,A. However, when the solubility to organic solvents, such as a glycerol and diethylene glucol, made it contain in a liquid constituent, and generally performed ink-jet record for a low reason and these polyvalent metallic salt was used, it was easy to produce a deposit at the nozzle nose of cam at which a drop blows off, and it had the trouble of becoming the cause of the blinding of a nozzle. Furthermore, when the liquid constituent which such polyvalent metallic salt contained was used for the record method of using the ink-jet method which records by making a drop breathing out by giving heat energy to ink and generating a foam, the above-mentioned polyvalent metal deposited on the exoergic heater, and there was also a trouble that the regurgitation of a drop will stop.

[0008]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is in view of the above-mentioned actual condition to offer the liquid constituent used for the outstanding image formation method which solved the technical problem of the six following points and the ink set which used this, the image formation method using these further, and image formation equipment. Namely, when ink-jet record to a regular paper is performed, it aims at satisfying the following recording characteristic.

(1) Character grace be good, having good fixing nature.

(2) Sufficient picture concentration is obtained and the homogeneity of a solid picture is high. Moreover, it aims at the following recording characteristic being satisfied at the time of the color picture formation especially to a regular paper.

(3) Bleeding should be prevented.

(4) Color-reproduction nature is good and a high definition record picture should be acquired.

(5) The record picture which has perfect water resistance should be acquired.

(6) Have lightfastness with a sufficient record picture.

[0009]

[Means for Solving the Problem] The above-mentioned purpose is attained by the following this inventions. That is, this invention is a liquid constituent used with the ink for forming a picture, and are the image formation method using the ink set and these which are characterized by combining the liquid constituent and this liquid constituent which are characterized by making a metal coordination compound contain in a liquid medium, and ink, and image formation equipment which has the above-mentioned liquid constituent and an ink set.

[0010] In this invention, the purpose of this invention can be attained by mixing the liquid constituent which does not contain color material, such as a color and a pigment, and the ink which color material contains in the place which permeated a record in the paper or the recording paper, and depositing the color material in ink. That is, as a result of mixing the color which is the color material contained in ink and which has an anionic machine at least with the metal coordination compound contained in the liquid constituent on record media, such as the recording paper, the phenomenon in which the central metal in a metal coordination compound reacts with the color material in ink, and color material deposits occurs.

[0011] This phenomenon is a phenomenon from which it is enclosed by the ligand and the metal configured at the center separates from the center and which carries out salt formation (lake-

izing) to acidic groups which are anionic machines in a color molecule, such as a carboxyl group and a sulfonic group. Although it is known well that the lake color by which salt formation of a water soluble dye and the polyvalent metal was carried out, and they were produced is generally excellent in lightfastness, it excels in lightfastness like [ the lake ghost which deposits in this invention ] the lake color known conventionally. Moreover, the distributed process which was indispensable in case the conventional lake color was used as a color material of ink in this invention is not required, either, and by the same method as the case where the ink using the usual water soluble dye is used, since the blinding preventive measures of the nozzle which becomes important in case it uses for the ink-jet record method further are also good, they do not cause the fall of the reliability of ink regurgitation nature, either.

[0012] Furthermore, in this invention, when the color in which a lake-ized reaction advances promptly is used, generating of not only the lightfastness of a picture but the bleeding between different colors (record dot) in the record paper can also be prevented. This is because mixture of the ink in the boundary section is prevented by momentary deposit of the color in said lake-ized reaction time.

[0013] On the other hand, when advance of a lake-ized reaction uses a late color, the case where it is difficult to prevent generating of bleeding completely arises. In this invention, bleeding can be effectively prevented by making a high molecular compound contain [ in such a case ] further in a liquid constituent in addition to the aforementioned metal coordination compound. It is neutralized by the ion-interaction of the central metal of a ligand, and this is considered that mixture of the ink in the boundary section is prevented, as a result of this high molecular compound's adsorbing in the meeting object which is depositing and a huge floc's generating.

[0014] According to this invention, many of color compounds are established on the front face of record media, such as the recording paper, for a deposit of a color which was described above. For this reason, it becomes possible to solve simultaneously not only the improvement in the fixing nature of ink but problems, such as a strike-through (osmosis of the ink to the rear face of paper) of the color nonuniformity under improvement in the coloring nature of a record picture, and the influence of the fiber on the front face of paper, and ink.

[0015]

[Embodiments of the Invention] Next, the gestalt of desirable operation is mentioned and this invention is explained still in detail. First, the liquid constituent of this invention is described. Two of (2) high molecular compounds which are used besides a solvent object as a component which constitutes the liquid constituent of this invention further in addition to (1) metal coordination compound and this metal coordination compound are mentioned. In addition, color material, such as a color and a pigment, is not contained in this liquid constituent. Hereafter, the each is described.

[0016] (1) A metal coordination compound metal coordination compound is a compound generally enclosed by the electron donor (ligand) in which a certain kind of metal ion has the capacity to coordinate to this metal ion. As an element which constitutes the ligand in which such a metal ion and a coordinate linkage are possible, it is restricted to the thing belonging to the 5th group in a periodic table, and the 6th group, and N, O, P, S, etc. are the typical element. When the metal coordination compound by which the nitrogen atom and the oxygen atom are contained in the ligand especially in this invention is used, since the lake-ized reaction of a color advances promptly, it is desirable. It can divide roughly into what has one electron releasing group in one ligand (one molecule) (1 seat ligand), and a thing (multidentate ligand) with two or more electron releasing groups as a kind of ligand which consists of these elements. It classifies for every coordination number and the example of a ligand is given to the following table 1.

配位数	配位子種
1	アンモニア 水 酢酸 ハロゲン
2	グリシン エチレンジアミン プロピレンジアミン 乳酸
3	イミノジ酢酸 ジエチレントリアミン
4	ジヒドロキシエチルグリシン ヒドロキシエチルイミノジ酢酸 ニトリロ三酢酸
6	エチレンジアミン四酢酸 ヒドロキシエチルエチレンジアミン四酢酸
8	ジエチレントリアミン五酢酸
10	トリエチレンテトラミン六酢酸

[0017] Table 1: Example of ligand

In this invention, although the metal coordination compound which has a two or more-coordination number ligand can be used preferably among these, the metal coordination compound which has a three or more-coordination number ligand is used preferably. In addition, if the coordination number is the metal coordination compound which has two or more ligands, without, of course being limited to what has the ligand mentioned to Table 1, anything can be preferably used for the compound which can be used by this invention.

[0018] Moreover, although it is possible to have set to this invention and to also use a gap preferably as a metal ion (central metal) configured by ligand which was described above if it is polyvalent metal ion, the effect that aluminum ion, nickel ion, a copper ion, barium ion, calcium ion, iron ion, chromium ion, etc. raise the lightfastness of a color is greatly desirable especially. Although the liquid constituent of this invention is characterized by the metal coordination compound constituted by a ligand which was mentioned above, and the metal ion containing, it can be carried out to the foundation (edited by Chemical Society of Japan) of inorganic chemistry etc. by the conventional method of a publication about the production method of this metal coordination compound. Moreover, the amount of these metal coordination compound contained in a liquid constituent in this invention needs to determine the optimal range with the combination of the matter used respectively, although 0.05 – 8.0 % of the weight is generally a suitable range on weight criteria.

[0019] Moreover, in the liquid constituent of this invention, it is desirable to reduce the metal ion concentration in the state where it has not configured in the ligand which can be set among a liquid constituent and which was described above from the purposes, such as improvement in regurgitation durability at the time of making the blinding prevention in the nose of cam of an ink-jet head and heat energy act on ink and a solvent object, and recording by injecting these liquids. In case a metal coordination compound is produced by method which was described above as a method of reducing the metal ion concentration in the state where it has not configured in such a ligand, there is a method of making the reaction of a metal ion and a ligand fully perform, and generating of the metal ion in the state where it has not configured by this method can be prevented.

[0020] As for what [ especially ] has the formation-ized reaction of a coordination compound comparatively late like aluminum ion, chromium ion, etc., it is desirable to operate boiling etc. to reaction time. It becomes possible to reduce the metal ion concentration in the state where it has not configured by this. Moreover, since the ease of happening of this reaction is influenced by the solution pH of reaction time, it is good to adjust to optimal pH and to make it react in the combination of a metal and a ligand.

[0021] Next, (2) high molecular compounds which the liquid constituent of this invention can be



made to contain in addition to the above-mentioned metal coordination compound are explained. The role of the high molecular compound added to the liquid constituent of this invention is as above-mentioned to prevent the bleeding of the ink on a record medium still more effectively. Therefore, when generating of bleeding is not seen, it is not necessary to add only the above-mentioned metal coordination compound. However, it is desirable that in a lake-sized reaction using a late color etc. number average molecular weight makes 1,000 or more high molecular compounds contain further, and uses them into a liquid constituent. In order that 1,000 or more high molecular compounds may adsorb a meeting object and number average molecular weight may tend to form a huge floc, it is considered because bleeding can be prevented effectively.

[0022] As a high molecular compound which can be used for the liquid constituent of this invention, non-ion polymer, such as cation nature polymer; acrylamides, such as the poly allylamine hydrochloride, a polyamine sulfone hydrochloride, a polyvinyl amine hydrochloride, and chitosan acetate, polyvinyl alcohol, and a polyvinyl pyrrolidone, etc. can specifically be mentioned. Moreover, in addition to this, you may be the cation nature polymer which cation-ized a part of non-ionicity polymeric material. specifically, natural, although the copolymer of a vinyl pyrrolidone and the 4th class salt of amino alkyl acrylate, the copolymer of acrylamide and the 4th class salt of aminomethyl acrylamide, etc. can be mentioned — this invention — not being limited to the high molecular compound of these cannot be overemphasized

[0023] Furthermore, although it is perfect if the above-mentioned polymeric material and the polymeric material of cation nature are water-soluble, you may be a dispersing element like a latex or an emulsion. Although 0.05 – 20 % of the weight is a suitable range as an amount of these high molecular compounds contained in the liquid constituent of this invention, the combination of other matter used respectively needs to determine the optimal range.

[0024] Next, the component of others which constitute the liquid constituent of this invention is described concretely. The liquid constituent of this invention usually consists of an additive of solvent objects, such as water and a water-soluble organic solvent, and others besides (1) metal coordination compound which was described above, and (2) high molecular compounds added if needed. As a water-soluble organic solvent used by this invention Ketones [ , such as an amides; acetone, ], such as a dimethylformamide and a dimethylacetamide; A tetrahydrofuran, Ether, such as a dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, A propylene glycol, a butylene glycol, a triethylene glycol, 1, 2, 6-hexane triol, a thiodiglycol, a hexylene glycol, Alkylene glycol, such as a diethylene glycol; An ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol monomethyl ether and the triethylene-glycol monomethyl ether; Ethanol, A glycerol besides monohydric alcohol, such as isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol, a N-methyl-2-pyrrolidone, 1, 3-dimethyl-imidazolidinone, a triethanolamine, a sulfolane, a dimethyl SARUHOKI side, etc. are mentioned.

[0025] About the content of the above-mentioned water-soluble organic solvent, although there is especially no limit, let it preferably be 5 – 70% of the weight of a range still more preferably five to 60% of the weight. In addition, you may blend additives, such as a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, and an evaporation accelerator, with the liquid constituent of this invention if needed. Selection of a surfactant is important especially when adjusting the permeability of a liquid. The range suitable as physical properties of the liquid constituent of this invention is each range 0 – 60 dyne/cm and whose viscosity 3–12, and surface tension are 1–30cps near 25 degree C for pH.

[0026] Next, the ink which constitutes the ink set of this invention is explained. The ink used by this invention consists of the various additives added the aquosity solvent object which consists of the water used for usual ink as other components or water, and a water-soluble organic solvent that what is necessary is just a thing containing the water soluble dye which contains an anionic machine at least as a color material, and if needed, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc.

[0027] If it is the water-soluble acid dye indicated by the Color Index (COLOUR INDEX), direct dye, or a reactive dye as a water soluble dye containing the anionic machine used by this invention, there will be especially no limit. Moreover, if what does not have a publication in a

Color Index has an anionic machine, for example, a sulfone machine, a carboxyl group, etc., there will be especially no limit. Naturally in the water soluble dye said here, a thing with the pH dependency of solubility is also contained. What has a carboxyl group in a color molecule especially in respect of the ease of being generated of the lake-ized reaction between the above-mentioned metal coordination compound and a color is desirable.

[0028] The example of the above-mentioned color used by this invention is given to below. As a color used for yellow ink, the C.I. direct yellow 142, 144, and 86 and C.I. acid yellow 23 grade are mentioned, for example. As a color which the C.I. acid reds 92, 289, 35, and 37 and 52 grades are mentioned, and is used for cyano ink as a color used for Magenta ink, for example for example, as a color which the C.I. acid blues 9, 7, 103, 1, and 90, the C.I. direct blue 86, and 87,199 grades are mentioned, and is used for black ink For example, although the C.I. hood black 2 and C.I. direct black 52,154,195 grade are mentioned, this invention is not limited to these.

[0029] 0.1 – 10% of the weight of the whole ink of the amount of the above-mentioned color used by this invention is desirable. It is not desirable, in order that the possibility of nozzle clogging may come out depending on a color, if decipherment of the character printed when there was less amount used than 0.1 % of the weight is difficult and there is more amount used than 10 % of the weight.

[0030] The water-soluble organic solvent used for said liquid constituent as a water-soluble organic solvent used for ink can be used similarly. The same is said of the suitable range of the content in the inside of the ink of these organic solvents. Moreover, the same is said of the suitable physical-properties range of ink, and pH is each range 0 – 60 dyne/cm and whose viscosity 3–12, and surface tension are 1–30cps near 25 degree C. However, about surface tension, since it may be demonstrated more effectively [ direction / the effect of this invention ] having made surface tension of a liquid constituent lower than the surface tension of ink, it is desirable. The detail is not clear although it is thought that it will be because it is effective in the liquid constituent driven in previously making uniform wettability of the ink later driven in on a record medium such composition, then on a printing process about this reason.

[0031] in order [ moreover, ] to raise the effect of this invention further — ink — the above — explanation — you may add an anionic surfactant or an anionic anionic polymeric material besides a component the bottom Or you may use it, adjusting the aforementioned amphoteric surface active agent to pH beyond the isoelectric point. As an example of an anionic surfactant, general things, such as a carboxylate type, a sulfate type, a sulfonate type, and a phosphoric ester type, can be used satisfactory. Moreover, as an example of an anionic polymeric material, although an alkali meltable type resin, the thing which copolymerized the acrylic acid can specifically be mentioned to a part of sodium polyacrylate or macromolecule, of course, this invention is not limited to these.

[0032] It is not restricted especially about the record medium used in case the image formation method of this invention is enforced, and the so-called regular papers, such as a copy paper currently used from the former and bond paper, are used suitably. The coat paper and the bright film for OHP which were specially produced to ink-jet record, of course are also used suitably, and common paper of fine quality and common glossy paper are also suitably usable.

[0033] The image formation method of this invention consists of a process (B) which gives the ink which contains an anionic compound for a liquid constituent at least with the process (A) of a record medium made to adhere to an image formation field at least to the aforementioned record medium with an ink-jet method, and a record medium makes the liquid constituent and ink which were described above adhere to an image formation field together at least, and it forms a picture. In addition, in an image formation field here, it is contained also near the image formation field. An image formation field is a field where the dot of ink adheres, and the thing of a field which separated about 1–5 dots from the outside of the field where the dot of ink adheres is pointed out near the image formation field here. Moreover, when [ of a record medium ] you make it adhere to an image formation field at least, you may make any a liquid constituent and ink adhere previously. That is, the above-mentioned process (A) may be performed in advance of the above-mentioned process (B), and a process (A) may be performed after a process (B).

[0034] It is easy to be natural even if it is the method of making it adhere all over a record

medium with a spray, a roller, etc. as a method of making a liquid constituent adhering on a record medium. However, if a liquid constituent can be made to adhere alternatively and uniformly only near the image formation field where it adheres to ink, and the image formation field, more desirable image formation can be carried out. Therefore, in this invention, it is more desirable to use the ink-jet method as a method of making a liquid constituent adhering on a record medium which can perform such adhesion. Moreover, as an ink-jet method, especially since the thing of the method which is made to inject these drops from a nozzle by giving heat energy especially to ink and a liquid constituent although the thing of which method may be used, and records can carry out easily high-density record, high-speed record, highly minute record, etc., it is desirable.

[0035] Moreover, if adhesion of a up to [ the record medium of ink ] performs color record with the ink-jet method on which the above heat energy is made to act using an ink-jet method and the ink set which consists of ink of which color of yellow, a Magenta, cyanogen, black, red, blue, and green, and a liquid constituent of this invention although more preferably performed by the on-demand type ink-jet method, it is high speed and a high-density and high definition color picture can be formed easily. Under the present circumstances, as a combination of the color of the desirable ink used as an ink set, they are the set of three colors of yellow, a Magenta, and cyanogen, or the set of four colors which added black to these three colors. Subsequently, the recording device used for the image formation method of this invention is explained. As described above, a record signal is given to the ink of a recording head in this invention, and \*\*\*\*\* which breathes out a drop with the generated heat energy is desirable. The composition of the recording head which is the principal part of the equipment is shown in drawing 1 , drawing 2 , and drawing 3 .

[0036] A head 13 pastes up the glass and the ceramic which have the slot 14 which lets ink pass or a plastic sheet, and the exoergic head 15 (although the thin shape head is shown drawing, not limited to this) which has the exoergic resistor layer used for thermal recording, and is obtained. The exoergic head 15 consists of the good substrate 20 of thermolysis nature, such as the exoergic resistor layer 18 formed with the protective coat 16 formed by the silicon oxide etc., the aluminum electrode 17-1 and 17-2, Nichrome, etc., the accumulation layer 19, and an alumina.

[0037] Ink 21 is coming to the regurgitation orifice 22, and forms the meniscus 23 with the pressure P. Here, if an electrical signal joins an electrode 17-1 and 17-2, the field shown by n of the exoergic head 15 generates heat rapidly, and a foam will be generated in the ink 21 which has touched here, a meniscus 23 will project by the pressure, and it will become the ink globule 24 from the regurgitation orifice 22, and will fly toward a record medium 25. The schematic diagram of the recording head which put in order many nozzles shown in drawing 1 is shown in drawing 3 . This recording head sticks the same exoergic head 28 as what was explained in 27 and drawing 1 which have much passage, such as a glass plate, and is made. In addition, drawing 1 is the cross section of a head 13 along ink passage, and drawing 2 is a cross section in the A-B line of drawing 1 .

[0038] An example of the ink-jet recording device which included this head in drawing 4 is shown. In drawing 4 , 61 is a blade as a wiping member, and the end is held by the blade attachment component, turns into the fixed end, and makes the gestalt of a KARENCHI lever. A blade 61 is held with the gestalt which it has been arranged in the position contiguous to the record section by the recording head 65, and was projected in the moving trucking of a recording head 65 in this example. 62 is the cap of the delivery side of a recording head 65, it is arranged in the home position which adjoins a blade 61, moves in the direction perpendicular to the move direction of a recording head 65, contacts an ink delivery side, and is equipped with the composition which performs capping. Further 63 is an ink absorber which adjoins a blade 61 and is formed, and is held with the gestalt projected in the moving trucking of a recording head 65 like a blade 61. The regurgitation recovery section 64 is constituted by the aforementioned blade 61, a cap 62, and the ink absorber 63, and removal of the moisture of an ink delivery side, dust, etc. is performed by a blade 61 and the ink absorber 63.

[0039] The recording head which records on the record medium which counters the delivery side

which 65 has a regurgitation energy generation means and allotted the delivery by breathing out ink, and 66 are the carriage for carrying a recording head 65 and performing the movement. Carriage 66 engaged with the guide shaft 67 possible [ sliding ], and has connected a part of carriage 66 with the belt 69 driven by the motor 68 (not shown). Thereby, carriage 66 becomes movable [ in alignment with the guide shaft 67 ], and becomes movable [ the record section by the recording head 65, and its adjoining field ].

[0040] The insertion section for 51 inserting a record medium and 52 are ejection rollers driven by the motor (not shown). It is discharged to the eccentric section which arranged the eccentric roller 53 as the delivery side of a recording head 65 and the position which counters are fed with a record medium by these composition and record advances by it. Although the cap 62 of the regurgitation recovery section 64 has evacuated from the moving trucking of a recording head 65 in case a recording head 65 returns to a home position by record end etc. in the above-mentioned composition, the blade 61 is projected in moving trucking. Consequently, wiping of the delivery side of a recording head 65 is carried out. In addition, when a cap 62 performs capping in contact with the delivery side of a recording head 65, a cap 62 moves so that it may project in the moving trucking of a recording head.

[0041] When a recording head 65 moves to a record starting position from a home position, a cap 62 and a blade 61 are in the same position as the position at the time of said wiping. Consequently, also in this movement, wiping of the delivery side of a recording head 65 is carried out. Movement at the home position of the aforementioned recording head 65 moves to the home position which adjoined the record section at the predetermined intervals, not only the time of a record end and regurgitation recovery but while moving in a record section for record of a recording head 65, and the above-mentioned wiping is performed with this movement.

[0042] Drawing 5 is drawing showing an example of the ink cartridge 45 which held the ink supplied to a head through ink feed-zone material, for example, a tube. 40 is the ink hold section which held the ink for supply, for example, an ink bag, and the plug 42 made of rubber is formed at the nose of cam here. By inserting a needle (not shown) in this plug 42, the ink in the ink bag 40 is closed on a head, if supply is possible. 44 is an ink absorber which receives waste ink. As the ink hold section, that in which the liquid-facing surface with ink is formed with a polyolefine, especially polyethylene is desirable. \*\*\*\* shown not only in that from which the head and ink cartridge like the above became another object but in drawing 6 as an ink-jet recording device used by this invention — that with which they were united is also used suitably

[0043] In drawing 6, 70 is a record unit, the ink hold section which held ink into this, for example, an ink absorber, is contained, and the ink in this ink absorber has composition breathed out as an ink drop from the head section 71 which has two or more orifices. As a material of an ink absorber, polyurethane can be used, for example. 72 is an air free passage mouth for making the atmosphere open the interior of a record unit for free passage. This record unit 70 is replaced with and used for the recording head shown by drawing 4, and attachment and detachment of it are attained to carriage 66. In addition, in the recording device used for this invention, although the ink-jet recording device which heat energy is made to act on ink above, and carries out the regurgitation of the ink drop was mentioned as the example, the ink-jet recording device of the piezo method which uses a piezoelectric device can be used similarly.

[0044] Now, in enforcing the record method of this invention, it uses the recording device which arranged five pieces in on carriage 80 for the recording head shown for example, in aforementioned drawing 3. Drawing 7 is the example. 81, 82, 83, and 84 are the recording heads for carrying out the regurgitation of the ink of yellow, Magenta, cyanogen, and black each color, respectively. Moreover, 85 is a head which carries out the regurgitation of the liquid constituent. These heads are arranged at said recording device, and carry out the regurgitation of the ink and the liquid constituent of each color according to a record signal. Although drawing 7 showed the example which used five recording heads, as it is not limited to this and shown in drawing 8, it is also desirable to divide a liquid flow channel and to carry out the regurgitation of yellow ink, Magenta ink, cyano ink, black ink, and the liquid constituent by one long recording head.

[0045]

[Example] An example is given to below and this invention is further explained to it concretely. In

addition, as long as there is no notice especially, there are weight criteria among a sentence altogether with the "section" or "%."

[0046] an example 1 — first, after carrying out the mixed dissolution of the following component, pressure filtration was carried out in the membrane filter (tradename; a FURORO pore filter, Sumitomo Electric Industries make) whose pore size is 0.22 micrometers, the metal ion which has not configured in liquid by reverse osmosis further was removed, and the colorless liquid constituent M-1 was obtained pH at this time was adjusted to 4.0. In addition, the amount of the water in a liquid constituent and ink was adjusted so that total of a constituent might become the 100 sections.

[0047]

Component of M-1 — metal coordination compound (aluminum-ethylenediaminetetraacetic acid coordination compound)

Section [ 1.0 / ] — Acrylamide Polymer 0.5 Sections — Thiodiglycol 15.0 Sections — Water

Remainder [0048] Next, the following component was mixed, pressure filtration was carried out in the membrane filter (tradename; a FURORO pore filter, Sumitomo Electric Industries make) whose pore size is 0.22 micrometers further, and yellow, a Magenta, cyanogen and each ink (1)-Y of black, (1)-M, (1)-C, and (1)-K were obtained. Composition of ink (1)-Y of yellow — C.I. direct yellow 142 The three sections — thiodiglycol The 12 sections — ASECHIRE Norian EH (Kawaken Fine Chemicals make) The 0.05 sections — water Remainder [0049] It is the same composition as (1)-Y except having replaced the composition color of ink (1)-M of a Magenta with the C.I. acid red 92 of the 3.5 sections from the C.I. direct yellow 142 of the three sections.

It is the same composition as (1)-Y except having replaced the composition color of ink (1)-C of cyanogen with the C.I. acid blue 9 of the 2.7 sections from the C.I. direct yellow 142 of the three sections.

It is the same composition as (1)-Y except having replaced the composition color of ink (1)-K of black with the C.I. hood black 2 from the C.I. direct yellow 142.

[0050] Next, it recorded on a commercial copy paper and commercial bond paper using the liquid constituent obtained as mentioned above and the ink of each color. The color picture was formed using five recording heads shown in drawing 7 using the recording device same as a used ink-jet recording device as what was shown in drawing 4. In addition, the recording head used here had the recording density of 360dpi, and set drive frequency to 5kHz as drive conditions, and the regurgitation volume per dot was 40pl(s). These record conditions are unified through the example of this invention. Moreover, the environmental condition in the case of a printing test is unified into RH 25 degrees C / 55%.

[0051] Evaluation of a record picture was performed by the following method.

1. The picture concentration solid picture was formed in a liquid constituent and black ink, and the reflection density after 12-hour neglect was measured by reflection density meter Macbeth RD 915 (made in Macbeth). The error criterion is as follows.

O : — reflection density — more than 1.25\*: — reflection density — 1.15–1.24x: — reflection density — 1.14 [0052] or less 2. Using a character grace liquid constituent and black ink, the alphanumeric character of black was recorded and viewing estimated. About the thing of the level not more than it, it considered as x, having used as O that in which feathering is not conspicuous.

[0053] 3. The solid section was adjacently recorded using the ink of each color of a bleeding liquid constituent, yellow, MAZENDA, cyanogen, and black, and the grade of the bleeding in the boundary section of each color was observed by viewing. What has bleeding in satisfactory level on parenchyma was made into O, and the thing of the level not more than it was taken as x.

4. Xenon light was irradiated for 50 hours at the record picture acquired by the evaluation examination of the picture lightfastness above 1, 2, and 3, and the survival rate (%) of the reflection density (OD value) in irradiation order was measured. OD survival rate made O 90% or more of thing, and the following [ it ] were taken as x.

[0054] 5. The recording head which showed the continuation regurgitation nature liquid constituent to drawing 7 was used, 100,000,000 times of pulse trains were given, and regurgitation durability was evaluated. What was able to perform the regurgitation continuously

was made into O till the test end, and what is in the middle of an examination and the regurgitation stopped was made into x. The number of nozzles used for the examination was used as three nozzles per one head. In addition, in the example of this invention, the adhesion field to the record medium of a liquid constituent is the same field as the image formation field of ink, it corresponds to the portion by which ink is driven into the record medium by 1:1, and the liquid constituent is driven into it. Furthermore, the printing direction is a uni directional and the liquid constituent is always driven in ahead of ink.

[0055] If it removed having not used the liquid constituent used in the example of comparison 1 example 1, record and the evaluation examination were performed completely like the example 1. The result of an evaluation examination of an example 1 and the example 1 of comparison is collectively indicated to Table 2. To the good result having been obtained by each about each evaluation of picture concentration, character grace, bleeding, and lightfastness, in the example 1 of comparison, only the low concentration picture was acquired, but bleeding occurred, and, moreover, it was inferior also to the lightfastness of a picture with the example 1 so that clearly from Table 2.

[0056] Table 2: Evaluation result of example 1 and example 1 of comparison

評価項目	実施例 1	比較例 1
画像濃度	○	×
文字品位	○	○
ブリーディング	○	×
画像耐光性	○	×
連続吐出性	○	×

[0057] Examples 2-6, next the component indicated to Table 3 were used, the liquid constituent and ink which consist of components shown in Table 4 were produced, and record and an evaluation examination of examples 2-6 were performed completely like the example 1. However, the same component as an example 1 is contained about components other than the component indicated in Table 4. Consequently, the good result was obtained by each about each evaluation of picture concentration, character grace, bleeding, and lightfastness like [ examples / 2-6 ] the case of the example 1 indicated to Table 2.

[0058] Table 3: Metal coordination compound used for examples 2-6 of this invention

番号	金属配位化合物	製造方法	構造
1	ニッケル-ヒドロキシエチレンジアミン四酢酸配位化合物	HEDTA (商品名、キレスト(株)製) とニッケルを等量 (1 モル : 1 モル) 混合したもの	$  \begin{array}{c}  \text{HOCH}_2\text{CH}_2 \\  \diagup \quad \diagdown \\  \text{NCH}_2\text{CH}_2\text{N} \\  \diagdown \quad \diagup \\  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \\  \text{CH}_2\text{COOH}  \end{array}  + \text{Ni}  $ <p style="text-align: center;">HEDTA</p>
2	銅-ニトリロ三酢酸配位化合物	NTA (商品名、キレスト(株)製) と銅を等量 (1 モル : 1 モル) 混合したもの	$  \begin{array}{c}  \text{CH}_2\text{COOH} \\  \diagup \\  \text{N} \\  \diagdown \\  \text{CH}_2\text{COOH} \\  \text{CH}_2\text{COOH}  \end{array}  + \text{Cu}  $ <p style="text-align: center;">NTA</p>
3	バリウム-ジエチレントリアミン五酢酸配位化合物	TTHA (商品名、キレスト(株)製) とバリウムを等量 (1 モル : 1 モル) 混合したもの	$  \begin{array}{c}  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \\  \diagdown \quad \diagup \quad \diagdown \quad \diagup \\  \text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N} \\  \diagup \quad \diagdown \quad \diagup \quad \diagdown \\  \text{HOOCCH}_2 \quad \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \quad \text{CH}_2\text{COOH}  \end{array}  + \text{Ba}  $ <p style="text-align: center;">TTHA</p>
4	アルミニウム-ヒドロキシエチレンジアミン四酢酸配位化合物	HEDTA (商品名、キレスト(株)製) とアルミニウムを等量 (1 モル : 1 モル) 混合したもの	$  \begin{array}{c}  \text{HOCH}_2\text{CH}_2 \\  \diagup \quad \diagdown \\  \text{NCH}_2\text{CH}_2\text{N} \\  \diagdown \quad \diagup \\  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \\  \text{CH}_2\text{COOH}  \end{array}  + \text{Al}  $ <p style="text-align: center;">HEDTA</p>

[0059] Table 4: Composition table of liquid constituent of examples 2-6

実施例	金属配位化合物	金属配位化合物含有量 (w t %)	その他の組成	液体組成物の pH
2	No.1	2.0	実施例 1 と同じ	6.0
3	No.2	1.5	実施例 1 と同じ	5.0
4	No.3	0.5	実施例 1 と同じ	8.0
5	No.4	1.2	実施例 1 と同じ	3.8
6	No.1	1.8	実施例 1 と同じ	6.0

[0060]

[Effect of the Invention] As explained above, when performing color ink-jet record to a regular paper according to this invention, picture concentration and character grace are high, and bleeding does not occur, but the picture with which were satisfied of good lightfastness can be acquired. In addition, the liquid constituent of this invention is excellent also in continuation regurgitation nature.

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] about the technology of reducing the so-called color bleeding (phenomenon) produced when forming a color picture in a regular paper, and acquiring the existing ink picture which is water resistance, this invention is divided and relates to the image formation method and image formation equipment using the liquid constituent applied in the image formation using the ink-jet method, the ink set which combined ink with this, and these

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PRIOR ART

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[Description of the Prior Art] The ink-jet record method makes an ink globule fly, and records by making ink adhere on record media, such as paper. According to the ink-jet record method of a method of making a drop breathing out by giving heat energy to ink, using an electric thermal-conversion object as a \*\*\*\* energy supply means currently especially indicated in JP,61-59912,B and JP,61-59914,B, and generating air bubbles, high-density multi-orifice-ization of a recording head can be realized easily, and high-speed record of high resolution and a quality picture is attained.

[0003] However, ink used for the conventional ink-jet record, Water was made into the principal component, and since what contained water-soluble high boilers, such as a glycol, for the purpose, such as dryness prevention and blinding prevention, in this was common, when recording using such ink, using a regular paper as a record medium, the problem of the uneven picture presumed not to obtain the fixing nature of sufficient picture or to be based on the uneven distribution of the loading material in a record-medium front face or a sizing compound occurring had arisen. Moreover, in order that the ink of two or more colors might pile up one after another before fixing to each color ink completely in the paper which is a record medium when it is going to obtain especially a color picture, in the unique boundary portion of a picture, there was also a problem that a color did not spread or the picture which should be mixed unevenly (this phenomenon is hereafter called bleeding), and should be satisfied was not acquired.

[0004] On the other hand, as a means which raises the fixing nature of a picture, adding the compound which raises the permeability of a surfactant etc. into ink is indicated by JP,55-65269,A. Moreover, using for JP,55-66976,A the ink which made the volatile solvent the subject is indicated. however, by the former method, as a result of the permeability to record Kaminaka of ink increasing, in order that the recording paper may be deep and color material may also carry out until osmosis with the ink of what can be raised to some extent about fixing nature and bleeding-proof nature, un-arranging [ of picture concentration and saturation falling ] occurs In addition, as a result of also generating the breadth to the longitudinal direction of ink, problems, such as a fall of the sharpness of the edge of a picture and a fall of a definition, are also generated simultaneously. In addition, the blinding by evaporation of the solvent in the nozzle section of a recording head to the former which was described above on the other hand in the case of the latter is easy to generate and is not desirable inconvenient.

[0005] Furthermore, the method of making the liquid constituent which has the function in which a formation picture becomes good in order to improve the various troubles mentioned above adhere on a record medium in advance of injection of ink is indicated. For example, after making the liquid constituent which the organic compound which has two or more cation nature machines per molecule contained adhere on a record medium in advance of injection of ink, the method of recording in the ink which the anionic color contained is indicated by JP,63-299971,A.

[0006] Moreover, the method of injecting the liquid constituent containing basic polymer in advance of record of ink is indicated by JP,63-60783,A and JP,64-63185,A. however, the above — in order that any method might use the polymer which has a cation nature machine, there

was a trouble of reducing the lightfastness of a color remarkably  
[0007] On the other hand, in advance of grant of the ink to a record medium, the compound formed of the ionic bond between polyvalent metallic salt, i.e., various metal ions, and anions, such as a halogenated compound and an organic acid, is beforehand given on the record medium, and the method of forming a picture in ink after that is indicated by JP,63-299970,A and JP,5-202328,A. However, when the solubility to organic solvents, such as a glycerol and diethylene glucohol, made it contain in a liquid constituent, and generally performed ink-jet record for a low reason and these polyvalent metallic salt was used, it was easy to produce a deposit at the nozzle nose of cam at which a drop blows off, and it had the trouble of becoming the cause of the blinding of a nozzle. Furthermore, when the liquid constituent which such polyvalent metallic salt contained was used for the record method of using the ink-jet method which records by making a drop breathing out by giving heat energy to ink and generating a foam, the above-mentioned polyvalent metal deposited on the exoergic heater, and there was also a trouble that the regurgitation of a drop will stop.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] As explained above, when performing color ink-jet record to a regular paper according to this invention, picture concentration and character grace are high, and bleeding does not occur, but the picture with which were satisfied of good lightfastness can be acquired. In addition, the liquid constituent of this invention is excellent also in continuation  
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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is in view of the above-mentioned actual condition to offer the liquid constituent used for the outstanding image formation method which solved the technical problem of the six following points and the ink set which used this, the image formation method using these further, and image formation equipment. Namely, when ink-jet record to a regular paper is performed, it aims at satisfying the following recording characteristic.

- (1) Character grace be good, having good fixing nature.
- (2) Sufficient picture concentration is obtained and the homogeneity of a solid picture is high. Moreover, it aims at the following recording characteristic being satisfied at the time of the color picture formation especially to a regular paper.
- (3) Bleeding should be prevented.
- (4) Color-reproduction nature is good and a high definition record picture should be acquired.
- (5) The record picture which has perfect water resistance should be acquired.
- (6) Have lightfastness with a sufficient record picture.

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**MEANS**

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[Means for Solving the Problem] The above-mentioned purpose is attained by the following this inventions. That is, this invention is a liquid constituent used with the ink for forming a picture, and are the image formation method using the ink set and these which are characterized by combining the liquid constituent and this liquid constituent which are characterized by making a metal coordination compound contain in a liquid medium, and ink, and image formation equipment which has the above-mentioned liquid constituent and an ink set.

[0010] In this invention, the purpose of this invention can be attained by mixing the liquid constituent which does not contain color material, such as a color and a pigment, and the ink which color material contains in the place which permeated a record in the paper or the recording paper, and depositing the color material in ink. That is, as a result of mixing the color which is the color material contained in ink and which has an anionic machine at least with the metal coordination compound contained in the liquid constituent on record media, such as the recording paper, the phenomenon in which the central metal in a metal coordination compound reacts with the color material in ink, and color material deposits occurs.

[0011] This phenomenon is a phenomenon from which it is enclosed by the ligand and the metal configured at the center separates from the center and which carries out salt formation (lake-izing) to acidic groups which are anionic machines in a color molecule, such as a carboxyl group and a sulfonic group. Although it is known well that the lake color by which salt formation of a water soluble dye and the polyvalent metal was carried out, and they were produced is generally excellent in lightfastness, it excels in lightfastness like [ the lake ghost which deposits in this invention ] the lake color known conventionally. Moreover, the distributed process which was indispensable in case the conventional lake color was used as a color material of ink in this invention is not required, either, and by the same method as the case where the ink using the usual water soluble dye is used, since the blinding preventive measures of the nozzle which becomes important in case it uses for the ink-jet record method further are also good, they do not cause the fall of the reliability of ink regurgitation nature, either.

[0012] Furthermore, in this invention, when the color in which a lake-ized reaction advances promptly is used, generating of not only the lightfastness of a picture but the bleeding between different colors (record dot) in the record paper can also be prevented. This is because mixture of the ink in the boundary section is prevented by momentary deposit of the color in said lake-ized reaction time.

[0013] On the other hand, when advance of a lake-ized reaction uses a late color, the case where it is difficult to prevent generating of bleeding completely arises. In this invention, bleeding can be effectively prevented by making a high molecular compound contain [ in such a case ] further in a liquid constituent in addition to the aforementioned metal coordination compound. It is neutralized by the ion-interaction of the central metal of a ligand, and this is considered that mixture of the ink in the boundary section is prevented, as a result of this high molecular compound's adsorbing in the meeting object which is depositing and a huge floc's generating.

[0014] According to this invention, many of color compounds are established on the front face of record media, such as the recording paper, for a deposit of a color which was described above. For this reason, it becomes possible to solve simultaneously not only the improvement in the

fixing nature of ink but problems, such as a strike-through (osmosis of the ink to the rear face of paper) of the color nonuniformity under improvement in the coloring nature of a record picture, and the influence of the fiber on the front face of paper, and ink.

[0015]

[Embodiments of the Invention] Next, the gestalt of desirable operation is mentioned and this invention is explained still in detail. First, the liquid constituent of this invention is described. Two of (2) high molecular compounds which are used besides a solvent object as a component which constitutes the liquid constituent of this invention further in addition to (1) metal coordination compound and this metal coordination compound are mentioned. In addition, color material, such as a color and a pigment, is not contained in this liquid constituent. Hereafter, the each is described.

[0016] (1) A metal coordination compound metal coordination compound is a compound generally enclosed by the electron donor (ligand) in which a certain kind of metal ion has the capacity to coordinate to this metal ion. As an element which constitutes the ligand in which such a metal ion and a coordinate linkage are possible, it is restricted to the thing belonging to the 5th group in a periodic table, and the 6th group, and N, O, P, S, etc. are the typical element. When the metal coordination compound by which the nitrogen atom and the oxygen atom are contained in the ligand especially in this invention is used, since the lake-sized reaction of a color advances promptly, it is desirable. It can divide roughly into what has one electron releasing group in one ligand (one molecule) (1 seat ligand), and a thing (multidentate ligand) with two or more electron releasing groups as a kind of ligand which consists of these elements. It classifies for every coordination number and the example of a ligand is given to the following table 1.

配位数	配位子種
1	アンモニア 水 酢酸 ハロゲン
2	グリシン エチレンジアミン プロピレンジアミン 乳酸
3	イミノジ酢酸 ジエチレントリアミン
4	ジヒドロキシエチルグリシン ヒドロキシエチルイミノジ酢酸 ニトリロ三酢酸
6	エチレンジアミン四酢酸 ヒドロキシエチルエチレンジアミン四酢酸
8	ジエチレントリアミン五酢酸
10	トリエチレントトラミン六酢酸

[0017] Table 1: Example of ligand

In this invention, although the metal coordination compound which has a two or more-coordination number ligand can be used preferably among these, the metal coordination compound which has a three or more-coordination number ligand is used preferably. In addition, if the coordination number is the metal coordination compound which has two or more ligands, without, of course being limited to what has the ligand mentioned to Table 1, anything can be preferably used for the compound which can be used by this invention.

[0018] Moreover, although it is possible to have set to this invention and to also use a gap preferably as a metal ion (central metal) configured by ligand which was described above if it is polyvalent metal ion, the effect that aluminum ion, nickel ion, a copper ion, barium ion, calcium ion, iron ion, chromium ion, etc. raise the lightfastness of a color is greatly desirable especially. Although the liquid constituent of this invention is characterized by the metal coordination compound constituted by a ligand which was mentioned above, and the metal ion containing, it can be carried out to the foundation (edited by Chemical Society of Japan) of inorganic

chemistry etc. by the conventional method of a publication about the production method of this metal coordination compound. Moreover, the amount of these metal coordination compound contained in a liquid constituent in this invention needs to determine the optimal range with the combination of the matter used respectively, although 0.05 – 8.0 % of the weight is generally a suitable range on weight criteria.

[0019] Moreover, in the liquid constituent of this invention, it is desirable to reduce the metal ion concentration in the state where it has not configured in the ligand which can be set among a liquid constituent and which was described above from the purposes, such as improvement in \*\*\*\* durability at the time of making the blinding prevention in the nose of cam of an ink-jet head and heat energy act on ink and a solvent object, and recording by injecting these liquids. In case a metal coordination compound is produced by method which was described above as a method of reducing the metal ion concentration in the state where it has not configured in such a ligand, there is a method of making the reaction of a metal ion and a ligand fully perform, and generating of the metal ion in the state where it has not configured by this method can be prevented.

[0020] As for what [ especially ] has the formation-ized reaction of a coordination compound comparatively late like aluminum ion, chromium ion, etc., it is desirable to operate boiling etc. to reaction time. It becomes possible to reduce the metal ion concentration in the state where it has not configured by this. Moreover, since the ease of happening of this reaction is influenced by the solution pH of reaction time, it is good to adjust to optimal pH and to make it react in the combination of a metal and a ligand.

[0021] Next, (2) high molecular compounds which the liquid constituent of this invention can be made to contain in addition to the above-mentioned metal coordination compound are explained. The role of the high molecular compound added to the liquid constituent of this invention is as above-mentioned to prevent the bleeding of the ink on a record medium still more effectively. Therefore, when generating of bleeding is not seen, it is not necessary to add only the above-mentioned metal coordination compound. However, it is desirable that in a lake-ized reaction using a late color etc. number average molecular weight makes 1,000 or more high molecular compounds contain further, and uses them into a liquid constituent. In order that 1,000 or more high molecular compounds may adsorb a meeting object and number average molecular weight may tend to form a huge floc, it is considered because bleeding can be prevented effectively.

[0022] As a high molecular compound which can be used for the liquid constituent of this invention, non-ion polymer, such as cation nature polymer; acrylamides, such as the poly allylamine hydrochloride, a polyamine sulfone hydrochloride, a polyvinyl amine hydrochloride, and chitosan acetate, polyvinyl alcohol, and a polyvinyl pyrrolidone, etc. can specifically be mentioned. Moreover, in addition to this, you may be the cation nature polymer which cation-ized a part of non-ionicity polymeric material. specifically, natural, although the copolymer of a vinyl pyrrolidone and the 4th class salt of amino alkyl acrylate, the copolymer of acrylamide and the 4th class salt of aminomethyl acrylamide, etc. can be mentioned — this invention — not being limited to the high molecular compound of these cannot be overemphasized

[0023] Furthermore, although it is perfect if the above-mentioned polymeric material and the polymeric material of cation nature are water-soluble, you may be a dispersing element like a latex or an emulsion. Although 0.05 – 20 % of the weight is a suitable range as an amount of these high molecular compounds contained in the liquid constituent of this invention, the combination of other matter used respectively needs to determine the optimal range.

[0024] Next, the component of others which constitute the liquid constituent of this invention is described concretely. The liquid constituent of this invention usually consists of an additive of solvent objects, such as water and a water-soluble organic solvent, and others besides (1) metal coordination compound which was described above, and (2) high molecular compounds added if needed. As a water-soluble organic solvent used by this invention Ketones [ , such as an amides; acetone, ], such as a dimethylformamide and a dimethylacetamide; A tetrahydrofuran, Ether, such as a dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, A propylene glycol, a butylene glycol, a triethylene glycol, 1, 2, 6-hexane triol, a thiodiglycol, a hexylene glycol, Alkylene glycol, such as a diethylene glycol; An ethylene

glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol monomethyl ether and the triethylene-glycol monomethyl ether; Ethanol, A glycerol besides monohydric alcohol, such as isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol, a N-methyl-2-pyrrolidone, 1, 3-dimethyl-imidazolidinone, a triethanolamine, a sulfolane, a dimethyl SARUHOKI side, etc. are mentioned.

[0025] About the content of the above-mentioned water-soluble organic solvent, although there is especially no limit, let it preferably be 5 - 70% of the weight of a range still more preferably five to 60% of the weight. In addition, you may blend additives, such as a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, and an evaporation accelerator, with the liquid constituent of this invention if needed. Selection of a surfactant is important especially when adjusting the permeability of a liquid. The range suitable as physical properties of the liquid constituent of this invention is each range 0 - 60 dyne/cm and whose viscosity 3-12, and surface tension are 1-30cps near 25 degree C for pH.

[0026] Next, the ink which constitutes the ink set of this invention is explained. The ink used by this invention consists of the various additives added the aqueous solvent object which consists of the water used for usual ink as other components or water, and a water-soluble organic solvent that what is necessary is just a thing containing the water soluble dye which contains an anionic machine at least as a color material, and if needed, for example, a viscosity controlling agent, pH regulator, antiseptics, a surfactant, an antioxidant, etc.

[0027] If it is the water-soluble acid dye indicated by the Color Index (COLOUR INDEX), direct dye, or a reactive dye as a water soluble dye containing the anionic machine used by this invention, there will be especially no limit. Moreover, if what does not have a publication in a Color Index has an anionic machine, for example, a sulfone machine, a carboxyl group, etc., there will be especially no limit. Naturally in the water soluble dye said here, a thing with the pH dependency of solubility is also contained. What has a carboxyl group in a color molecule especially in respect of the ease of being generated of the lake-ized reaction between the above-mentioned metal coordination compound and a color is desirable.

[0028] The example of the above-mentioned color used by this invention is given to below. As a color used for yellow ink, the C.I. direct yellow 142, 144, and 86 and C.I. acid yellow 23 grade are mentioned, for example. As a color which the C.I. acid reds 92, 289, 35, and 37 and 52 grades are mentioned, and is used for cyano ink as a color used for Magenta ink, for example for example, as a color which the C.I. acid blues 9, 7, 103, 1, and 90, the C.I. direct blue 86, and 87,199 grades are mentioned, and is used for black ink For example, although the C.I. hood black 2 and C.I. direct black 52,154,195 grade are mentioned, this invention is not limited to these.

[0029] 0.1 - 10% of the weight of the whole ink of the amount of the above-mentioned color used by this invention is desirable. It is not desirable, in order that the possibility of nozzle clogging may come out depending on a color, if decipherment of the character printed when there was less amount used than 0.1 % of the weight is difficult and there is more amount used than 10 % of the weight.

[0030] The water-soluble organic solvent used for said liquid constituent as a water-soluble organic solvent used for ink can be used similarly. The same is said of the suitable range of the content in the inside of the ink of these organic solvents. Moreover, the same is said of the suitable physical-properties range of ink, and pH is each range 0 - 60 dyne/cm and whose viscosity 3-12, and surface tension are 1-30cps near 25 degree C. However, about surface tension, since it may be demonstrated more effectively [ direction / the effect of this invention ] having made surface tension of a liquid constituent lower than the surface tension of ink, it is desirable. The detail is not clear although it is thought that it will be because it is effective in the liquid constituent driven in previously making uniform wettability of the ink later driven in on a record medium such composition, then on a printing process about this reason.

[0031] in order [ moreover, ] to raise the effect of this invention further — ink — the above — explanation — you may add an anionic surfactant or an anionic anionic polymeric material besides a component the bottom Or you may use it, adjusting the aforementioned amphoteric surface active agent to pH beyond the isoelectric point. As an example of an anionic surfactant, general things, such as a carboxylate type, a sulfate type, a sulfonate type, and a phosphoric



ester type, can be used satisfactory. Moreover, as an example of an anionic polymeric material, although an alkali meltable type resin, the thing which copolymerized the acrylic acid can specifically be mentioned to a part of sodium polyacrylate or macromolecule, of course, this invention is not limited to these.

[0032] It is not restricted especially about the record medium used in case the image formation method of this invention is enforced, and the so-called regular papers, such as a copy paper currently used from the former and bond paper, are used suitably. The coat paper and the bright film for OHP which were specially produced to ink-jet record, of course are also used suitably, and common paper of fine quality and common glossy paper are also suitably usable.

[0033] The image formation method of this invention consists of a process (B) which gives the ink which contains an anionic compound for a liquid constituent at least with the process (A) of a record medium made to adhere to an image formation field at least to the aforementioned record medium with an ink-jet method, and a record medium makes the liquid constituent and ink which were described above adhere to an image formation field together at least, and it forms a picture. In addition, in an image formation field here, it is contained also near the image formation field. An image formation field is a field where the dot of ink adheres, and the thing of a field which separated about 1-5 dots from the outside of the field where the dot of ink adheres is pointed out near the image formation field here. Moreover, when [ of a record medium ] you make it adhere to an image formation field at least, you may make any a liquid constituent and ink adhere previously. That is, the above-mentioned process (A) may be performed in advance of the above-mentioned process (B), and a process (A) may be performed after a process (B).

[0034] It is easy to be natural even if it is the method of making it adhere all over a record medium with a spray, a roller, etc. as a method of making a liquid constituent adhering on a record medium. However, if a liquid constituent can be made to adhere alternatively and uniformly only near the image formation field where it adheres to ink, and the image formation field, more desirable image formation can be carried out. Therefore, in this invention, it is more desirable to use the ink-jet method as a method of making a liquid constituent adhering on a record medium which can perform such adhesion. Moreover, as an ink-jet method, especially since the thing of the method which is made to inject these drops from a nozzle by giving heat energy especially to ink and a liquid constituent although the thing of which method may be used, and records can carry out easily high-density record, high-speed record, highly minute record, etc., it is desirable.

[0035] Moreover, if adhesion of a up to [ the record medium of ink ] performs color record with the ink-jet method on which the above heat energy is made to act using an ink-jet method and the ink set which consists of ink of which color of yellow, a Magenta, cyanogen, black, red, blue, and green, and a liquid constituent of this invention although more preferably performed by the on-demand type ink-jet method, it is high speed and a high-density and high definition color picture can be formed easily. Under the present circumstances, as a combination of the color of the desirable ink used as an ink set, they are the set of three colors of yellow, a Magenta, and cyanogen, or the set of four colors which added black to these three colors. Subsequently, the recording device used for the image formation method of this invention is explained. As described above, a record signal is given to the ink of a recording head in this invention, and the method which carries out the regurgitation of the drop with the generated heat energy is desirable. The composition of the recording head which is the principal part of the equipment is shown in drawing 1 , drawing 2 , and drawing 3 .

[0036] A head 13 pastes up the glass and the ceramic which have the slot 14 which lets ink pass or a plastic sheet, and the exoergic head 15 (although the thin shape head is shown drawing, not limited to this) which has the exoergic resistor layer used for thermal recording, and is obtained. The exoergic head 15 consists of the good substrate 20 of thermolysis nature, such as the exoergic resistor layer 18 formed with the protective coat 16 formed by the silicon oxide etc., the aluminum electrode 17-1 and 17-2, Nichrome, etc., the accumulation layer 19, and an alumina.

[0037] Ink 21 is coming to the regurgitation orifice 22, and forms the meniscus 23 with the pressure P. Here, if an electrical signal joins an electrode 17-1 and 17-2, the field shown by n of

the exoergic head 15 generates heat rapidly, and a foam will be generated in the ink 21 which has touched here, a meniscus 23 will project by the pressure, and it will become the ink globule 24 from the regurgitation orifice 22, and will fly toward a record medium 25. The schematic diagram of the recording head which put in order many nozzles shown in drawing 1 is shown in drawing 3. This recording head sticks the same exoergic head 28 as what was explained in 27 and drawing 1 which have much passage, such as a glass plate, and is made. In addition, drawing 1 is the cross section of a head 13 along ink passage, and drawing 2 is a cross section in the A-B line of drawing 1.

[0038] An example of the ink-jet recording device which included this head in drawing 4 is shown. In drawing 4, 61 is a blade as a wiping member, and the end is held by the blade attachment component, turns into the fixed end, and makes the gestalt of a KARENCHI lever. A blade 61 is held with the gestalt which it has been arranged in the position contiguous to the record section by the recording head 65, and was projected in the moving trucking of a recording head 65 in this example. 62 is the cap of the delivery side of a recording head 65, it is arranged in the home position which adjoins a blade 61, moves in the direction perpendicular to the move direction of a recording head 65, contacts an ink delivery side, and is equipped with the composition which performs capping. Further 63 is an ink absorber which adjoins a blade 61 and is formed, and is held with the gestalt projected in the moving trucking of a recording head 65 like a blade 61. The regurgitation recovery section 64 is constituted by the aforementioned blade 61, a cap 62, and the ink absorber 63, and removal of the moisture of an ink delivery side, dust, etc. is performed by a blade 61 and the ink absorber 63.

[0039] The recording head which records on the record medium which counters the delivery side which 65 has a regurgitation energy generation means and allotted the delivery by breathing out ink, and 66 are the carriage for carrying a recording head 65 and performing the movement. Carriage 66 engaged with the guide shaft 67 possible [ sliding ], and has connected a part of carriage 66 with the belt 69 driven by the motor 68 (not shown). Thereby, carriage 66 becomes movable [ in alignment with the guide shaft 67 ], and becomes movable [ the record section by the recording head 65, and its adjoining field ].

[0040] The insertion section for 51 inserting a record medium and 52 are ejection rollers driven by the motor (not shown). It is discharged to the eccrisis section which arranged the eccrisis roller 53 as the delivery side of a recording head 65 and the position which counters are fed with a record medium by these composition and record advances by it. Although the cap 62 of the regurgitation recovery section 64 has evacuated from the moving trucking of a recording head 65 in case a recording head 65 returns to a home position by record end etc. in the above-mentioned composition, the blade 61 is projected in moving trucking. Consequently, wiping of the delivery side of a recording head 65 is carried out. In addition, when a cap 62 performs capping in contact with the delivery side of a recording head 65, a cap 62 moves so that it may project in the moving trucking of a recording head.

[0041] When a recording head 65 moves to a record starting position from a home position, a cap 62 and a blade 61 are in the same position as the position at the time of said wiping.

Consequently, also in this movement, wiping of the delivery side of a recording head 65 is carried out. Movement at the home position of the aforementioned recording head 65 moves to the home position which adjoined the record section at the predetermined intervals, not only the time of a record end and regurgitation recovery but while moving in a record section for record of a recording head 65, and the above-mentioned wiping is performed with this movement.

[0042] Drawing 5 is drawing showing an example of the ink cartridge 45 which held the ink supplied to a head through ink feed-zone material, for example, a tube. 40 is the ink hold section which held the ink for supply, for example, an ink bag, and the plug 42 made of rubber is formed at the nose of cam here. By inserting a needle (not shown) in this plug 42, the ink in the ink bag 40 is closed on a head, if supply is possible. 44 is an ink absorber which receives waste ink. As the ink hold section, that in which the liquid-facing surface with ink is formed with a polyolefine, especially polyethylene is desirable. \*\*\*\* shown not only in that from which the head and ink cartridge like the above became another object but in drawing 6 as an ink-jet recording device used by this invention — that with which they were united is also used suitably

[0043] In drawing 6 , 70 is a record unit, the ink hold section which held ink into this, for example, an ink absorber, is contained, and the ink in this ink absorber has composition breathed out as an ink drop from the head section 71 which has two or more orifices. As a material of an ink absorber, polyurethane can be used, for example. 72 is an air free passage mouth for making the atmosphere open the interior of a record unit for free passage. This record unit 70 is replaced with and used for the recording head shown by drawing 4 , and attachment and detachment of it are attained to carriage 66. In addition, in the recording device used for this invention, although the \*\* ink-jet recording device which heat energy is made to act on ink above, and breathes out an ink drop was mentioned as the example, the ink-jet recording device of the piezo method which uses a piezoelectric device can be used similarly.

[0044] Now, in enforcing the record method of this invention, it uses the recording device which arranged five pieces in on carriage 80 for the recording head shown for example, in aforementioned drawing 3 . Drawing 7 is the example. 81, 82, 83, and 84 are the recording heads of the \*\* sake which breathes out the ink of yellow, Magenta, cyanogen, and black each color, respectively. Moreover, 85 is a \*\* head which breathes out a liquid constituent. These heads are \*\* which is arranged at said recording device and breathes out the ink and the liquid constituent of each color according to a record signal. Although drawing 7 showed the example which used five recording heads, as it is not limited to this and shown in drawing 8 , \*\* which divides a liquid flow channel and breathes out yellow ink, Magenta ink, cyano ink, black ink, and a liquid constituent by one long recording head is also desirable.

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**EXAMPLE**

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[Example] An example is given to below and this invention is further explained to it concretely. In addition, as long as there is no notice especially, there are weight criteria among a sentence altogether with the "section" or "%."

[0046] an example 1 — first, after carrying out the mixed dissolution of the following component, pressure filtration was carried out in the membrane filter (tradename; a FURORO pore filter, Sumitomo Electric Industries make) whose pore size is 0.22 micrometers, the metal ion which has not configured in liquid by reverse osmosis further was removed, and the colorless liquid constituent M-1 was obtained pH at this time was adjusted to 4.0. In addition, the amount of the water in a liquid constituent and ink was adjusted so that total of a constituent might become the 100 sections.

[0047]

Component of M-1 — metal coordination compound (aluminum-ethylenediaminetetraacetic acid coordination compound)

Section [ 1.0 / ] — Acrylamide Polymer 0.5 Sections — Thiodiglycol 15.0 Sections — Water

Remainder [0048] Next, the following component was mixed, pressure filtration was carried out in the membrane filter (tradename; a FURORO pore filter, Sumitomo Electric Industries make) whose pore size is 0.22 micrometers further, and yellow, a Magenta, cyanogen and each ink (1)-Y of black, (1)-M, (1)-C, and (1)-K were obtained.

Composition of ink (1)-Y of yellow — C.I. direct yellow 142 The three sections — thiodiglycol The 12 sections — ASECHIRE Norian EH (Kawaken Fine Chemicals make) The 0.05 sections — water Remainder [0049] It is the same composition as (1)-Y except having replaced the composition color of ink (1)-M of a Magenta with the C.I. acid red 92 of the 3.5 sections from the C.I. direct yellow 142 of the three sections.

It is the same composition as (1)-Y except having replaced the composition color of ink (1)-C of cyanogen with the C.I. acid blue 9 of the 2.7 sections from the C.I. direct yellow 142 of the three sections.

It is the same composition as (1)-Y except having replaced the composition color of ink (1)-K of black with the C.I. hood black 2 from the C.I. direct yellow 142.

[0050] Next, it recorded on a commercial copy paper and commercial bond paper using the liquid constituent obtained as mentioned above and the ink of each color. The color picture was formed using five recording heads shown in drawing 7 using the recording device same as a used ink-jet recording device as what was shown in drawing 4. In addition, the recording head used here had the recording density of 360dpi, and set drive frequency to 5kHz as drive conditions, and the regurgitation volume per dot was 40pl(s). These record conditions are unified through the example of this invention. Moreover, the environmental condition in the case of a printing test is unified into RH 25 degrees C / 55%.

[0051] Evaluation of a record picture was performed by the following method.

1. The picture concentration solid picture was formed in a liquid constituent and black ink, and the reflection density after 12-hour neglect was measured by reflection density meter Macbeth RD 915 (made in Macbeth). The error criterion is as follows.

O : — reflection density — more than 1.25\*\* : — reflection density — 1.15–1.24x : — reflection

density — 1.14 [0052] or less 2. Using a character grace liquid constituent and black ink, the alphanumeric character of black was recorded and viewing estimated. About the thing of the level not more than it, it considered as x, having used as O that in which feathering is not conspicuous.

[0053] 3. The solid section was adjacently recorded using the ink of each color of a bleeding liquid constituent, yellow, MAZENDA, cyanogen, and black, and the grade of the bleeding in the boundary section of each color was observed by viewing. What has bleeding in satisfactory level on parenchyma was made into O, and the thing of the level not more than it was taken as x.

4. Xenon light was irradiated for 50 hours at the record picture acquired by the evaluation examination of the picture lightfastness above 1, 2, and 3, and the survival rate (%) of the reflection density (OD value) in irradiation order was measured. OD survival rate made O 90% or more of thing, and the following [ it ] were taken as x.

[0054] 5. The recording head which showed the continuation regurgitation nature liquid constituent to drawing 7 was used, 100,000,000 times of pulse trains were given, and regurgitation durability was evaluated. What was able to perform the regurgitation continuously was made into O till the test end, and what is in the middle of an examination and the regurgitation stopped was made into x. The number of nozzles used for the examination was used as three nozzles per one head. In addition, in the example of this invention, the adhesion field to the record medium of a liquid constituent is the same field as the image formation field of ink, it corresponds to the portion by which ink is driven into the record medium by 1:1, and the liquid constituent is driven into it. Furthermore, the printing direction is a uni directional and the liquid constituent is always driven in ahead of ink.

[0055] If it removed having not used the liquid constituent used in the example of comparison 1 example 1, record and the evaluation examination were performed completely like the example 1. The result of an evaluation examination of an example 1 and the example 1 of comparison is collectively indicated to Table 2. To the good result having been obtained by each about each evaluation of picture concentration, character grace, bleeding, and lightfastness, in the example 1 of comparison, only the low concentration picture was acquired, but bleeding occurred, and, moreover, it was inferior also to the lightfastness of a picture with the example 1 so that clearly from Table 2.

[0056] Table 2: Evaluation result of example 1 and example 1 of comparison

評価項目	実施例 1	比較例 1
画像濃度	○	×
文字品位	○	○
ブリーディング	○	×
画像耐光性	○	×
連続吐出性	○	×

[0057] Examples 2-6, next the component indicated to Table 3 were used, the liquid constituent and ink which consist of components shown in Table 4 were produced, and record and an evaluation examination of examples 2-6 were performed completely like the example 1. However, the same component as an example 1 is contained about components other than the component indicated in Table 4. Consequently, the good result was obtained by each about each evaluation of picture concentration, character grace, bleeding, and lightfastness like [ examples / 2-6 ] the case of the example 1 indicated to Table 2.

[0058] Table 3: Metal coordination compound used for examples 2-6 of this invention

番号	金属配位化合物	製造方法	構造
1	ニッケル-ヒドロキシエチレンジアミン四酢酸配位化合物	HEDTA (商品名、キレスト(株)製) とニッケルを等量 (1 モル: 1 モル) 混合したもの	$  \begin{array}{c}  \text{HOCH}_2\text{CH}_2 \quad \text{CH}_2\text{COOH} \\  \diagdown \quad \diagup \\  \text{NCH}_2\text{CH}_2\text{N} \\  \diagup \quad \diagdown \\  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH}  \end{array}  + \text{Ni}  $ <p style="text-align: center;">HEDTA</p>
2	銅-ニトリロ三酢酸配位化合物	NTA (商品名、キレスト(株)製) と銅を等量 (1 モル: 1 モル) 混合したもの	$  \begin{array}{c}  \text{CH}_2\text{COOH} \\  \diagdown \\  \text{N} \\  \diagup \\  \text{CH}_2\text{COOH} \\  \diagdown \\  \text{CH}_2\text{COOH}  \end{array}  + \text{Cu}  $ <p style="text-align: center;">NTA</p>
3	バリウム-ジェチレントリアミン五酢酸配位化合物	TTHA (商品名、キレスト(株)製) とバリウムを等量 (1 モル: 1 モル) 混合したもの	$  \begin{array}{c}  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \\  \diagdown \quad \diagup \\  \text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N} \\  \diagup \quad \diagdown \quad \diagup \quad \diagdown \\  \text{HOOCCH}_2 \quad \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \quad \text{CH}_2\text{COOH}  \end{array}  + \text{Ba}  $ <p style="text-align: center;">TTHA</p>
4	アルミニウム-ヒドロキシエチレンジアミン四酢酸配位化合物	HEDTA (商品名、キレスト(株)製) とアルミニウムを等量 (1 モル: 1 モル) 混合したもの	$  \begin{array}{c}  \text{HOCH}_2\text{CH}_2 \quad \text{CH}_2\text{COOH} \\  \diagdown \quad \diagup \\  \text{NCH}_2\text{CH}_2\text{N} \\  \diagup \quad \diagdown \\  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH}  \end{array}  + \text{Al}  $ <p style="text-align: center;">HEDTA</p>

[0059] Table 4: Composition table of liquid constituent of examples 2-6

実施例	金属配位化合物	金属配位化合物含有量 (wt %)	その他の組成	液体組成物の pH
2	No.1	2.0	実施例 1 と同じ	6.0
3	No.2	1.5	実施例 1 と同じ	5.0
4	No.3	0.5	実施例 1 と同じ	8.0
5	No.4	1.2	実施例 1 と同じ	3.8
6	No.1	1.8	実施例 1 と同じ	6.0

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is drawing of longitudinal section of the head section of an ink-jet recording device.

[Drawing 2] It is the cross-sectional view of the head section of an ink-jet recording device.

[Drawing 3] It is the appearance perspective diagram of the head section of an ink-jet recording device.

[Drawing 4] It is the perspective diagram showing an example of an ink-jet recording device.

[Drawing 5] It is drawing of longitudinal section of an ink cartridge.

[Drawing 6] It is the perspective diagram of a record unit.

[Drawing 7] It is the perspective diagram having shown the Records Department which two or more recording heads used in the example of this invention arranged.

[Drawing 8] It is the perspective diagram of another recording head used for this invention.

[Description of Notations]

13: Head

14: Ink slot

15 28: Exoergic head

16: Protective coat

17: Aluminum electrode

18: Exoergic resistor layer

19: Accumulation layer

20: Substrate

21: Ink

22: Regurgitation orifice (micropore)

23: Meniscus

24: Ink globule

25: Record medium

26: Multi-slot

27: Glass plate

40: Ink bag

42: The plug made of rubber

44: Ink absorber

45: Ink cartridge

51: Feed section

52: Ejection roller

52: Delivery roller

61: Blade

62: Cap

63: Ink absorber

64: Regurgitation recovery section

65: Recording head

66: Carriage

- 67: Guide shaft
- 68: Motor
- 69: Belt
- 70: Record unit
- 71: Head section
- 72: Air free passage mouth
- 80: Carriage
- 81: The recording head for carrying out the regurgitation of the ink of yellow
- 82: The recording head for carrying out the regurgitation of the ink of a Magenta
- 83: The recording head for carrying out the regurgitation of the ink of cyanogen
- 84: The recording head for carrying out the regurgitation of the ink of black
- 85: The recording head for carrying out the regurgitation of the liquid constituent

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[Translation done.]



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(54) 【発明の名称】 液体組成物、インクセット、これらを用いた画像形成方法及び画像形成装置

(57) 【要約】

【課題】 定着性及び文字品位が良好で、十分な画像濃度を得られ、ベタ画像の均一性が高く、又、カラー画像形成において、ブリードレス、高再現性、高精細性、耐水性及び耐光性を有する記録画像を提供すること。

【解決手段】 液体組成物中に金属配位化合物を含有させたことを特徴とする液体組成物、該液体組成物とインクとを組み合わせたことを特徴とするインクセット、これらを用いる画像形成方法、及び上記液体組成物とインクセットを有する画像形成装置。

(2)

## 【特許請求の範囲】

【請求項1】 画像を形成するためのインクと共に使用する液体組成物であって、液媒体中に金属配位化合物を含有させたことを特徴とする液体組成物。

【請求項2】 前記金属配位化合物を構成する配位子が2以上の配位数を有する請求項1に記載の液体組成物。

【請求項3】 前記金属配位化合物を構成する配位子が3以上の配位数を有する請求項1に記載の液体組成物。

【請求項4】 前記配位子が、グリシン、エチレンジアミン、プロピレンジアミン、乳酸、イミノジ酢酸、ジエチレントリアミン、ジヒドロキシエチルグリシン、ヒドロキシエチルイミノジ酢酸、ニトリロ三酢酸、エチレンジアミン四酢酸、ヒドロキシエチルエチレンジアミン四酢酸、ジエチレントリアミン五酢酸、トリエチレンテトラミン六酢酸の中から選ばれる何れかである請求項2又は請求項3に記載の液体組成物。

【請求項5】 前記金属配位化合物を構成する金属イオンが、アルミニウムイオン、ニッケルイオン、銅イオン、バリウムイオン、カルシウムイオン、鉄イオン又はクロムイオンの何れかである請求項1に記載の液体組成物。

【請求項6】 更に数平均分子量が1,000以上の高分子化合物を含む請求項1に記載の液体組成物。

【請求項7】 前記金属配位化合物を0.05～8.0重量%の範囲で含む請求項1に記載の液体組成物。

【請求項8】 前記液媒体として水及び水溶性有機溶剤を含む請求項1に記載の液体組成物。

【請求項9】 前記高分子化合物を0.05～20重量%の範囲で含む請求項6に記載の液体組成物。

【請求項10】 請求項1～9の何れかに記載の液体組成物と、イエロー、マゼンタ、シアン、ブラック、レッド、ブルー、グリーンの少なくとも1つのインクとを組み合わせたことを特徴とするインクセット。

【請求項11】 請求項1～9の何れかに記載の液体組成物と、イエロー、マゼンタ、シアンの3色のインクとを組み合わせたことを特徴とするインクセット。

【請求項12】 請求項1～9の何れかに記載の液体組成物と、イエロー、マゼンタ、シアン及びブラックの4色のインクとを組み合わせたことを特徴とするインクセット。

【請求項13】 インクがアニオン性化合物を含む請求項10～12の何れかに記載のインクセット。

【請求項14】 インクがアニオン性基を有する水溶性染料を含む請求項10～12の何れかに記載のインクセット。

【請求項15】 前記液体組成物と前記インクとを分離して収納した請求項10～12の何れかに記載のインクセット。

【請求項16】 請求項1～9の何れかに記載の液体組成物を記録媒体の少なくとも画像形成領域に付着させる

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工程(A)と、少なくともアニオン性化合物を含有するインクをインクジェット方式により前記記録媒体に付与する工程(B)を含むことを特徴とする画像形成方法。

【請求項17】 前記インクジェット方式がオンデマンド型インクジェット方式である請求項16に記載の画像形成方法。

【請求項18】 前記液体組成物をインクジェット方式により記録媒体に付着させる請求項16に記載の画像形成方法。

10 【請求項19】 前記インクジェット方式が熱エネルギーを作用させるインクジェット方式である請求項16～18の何れかに記載の画像形成方法。

【請求項20】 工程(A)を工程(B)に先だって行なう請求項16に記載の画像形成方法。

【請求項21】 工程(A)を工程(B)の後に行なう請求項16に記載の画像形成方法。

【請求項22】 請求項10～15の何れかに記載のインクセットとインクジェット手段とを有することを特徴とする画像形成装置。

20 【請求項23】 請求項1～9の何れかに記載の液体組成物の収納部及び吐出手段を有する第一の記録ユニットと、少なくともアニオン性化合物を含有するインクの収納部及び吐出手段を有する第二の記録ユニットとを備えたことを特徴とする画像形成装置。

【請求項24】 前記吐出手段がインクジェット手段である請求項23に記載の画像形成装置。

【請求項25】 前記インクジェット手段が熱エネルギーを作用させてインク滴を形成する手段である請求項22又は請求項24に記載の画像形成装置。

30 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、普通紙にカラー画像を形成するとき生じる、所謂、カラー・ブリーディング(現象)を低減し、且つ耐水性のあるインク画像を得る技術に関し、とりわけ、インクジェット方式を利用した画像形成において適用される液体組成物、これにインクを組み合わせたインクセット、これらを用いた画像形成方法及び画像形成装置に関する。

## 【0002】

40 【従来の技術】インクジェット記録方法は、インク小滴を飛翔させ、紙等の記録媒体上にインクを付着させて記録を行うものである。特に、特公昭61-59912号公報及び特公昭61-59914号公報において開示されている、吐出エネルギーの供給手段として電気熱変換体を用いて熱エネルギーをインクに与えて気泡を発生させることにより液滴を吐出させる方式のインクジェット記録方法によれば、記録ヘッドの高密度マルチオリフィス化を容易に実現することができ、且つ高解像度及び高品質の画像の高速記録が可能となる。

50 【0003】しかしながら、従来のインクジェット記録

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に用いられるインクは、水を主成分とし、これに乾燥防止や目詰まり防止等の目的でグリコール等の水溶性高沸点溶剤を含有したものが一般的であるため、このようなインクを用い、記録媒体として普通紙を用いて記録を行った場合には、十分な画像の定着性が得られなかったり、記録媒体表面における填料やサイズ剤の不均一な分布によると推定される不均一画像が発生する等の問題が生じていた。又、特にカラー画像を得ようとする場合には、夫々のカラーインクが記録媒体である紙上に完全に定着される以前に複数の色のインクが次々と重ねられるため、異色の画像の境界部分では、色が滲んだり、不均一に混ざり合い（以下、この現象をブリーディングと呼ぶ）満足すべき画像が得られないという問題もあった。

【0004】これに対し画像の定着性を高める手段として、特開昭55-65269号公報には、インク中に界面活性剤等の浸透性を高める化合物を添加することが開示されている。又、特開昭55-66976号公報には、揮発性溶剤を主体としたインクを用いることが開示されている。しかし、前者の方法では、インクの記録紙中への浸透性が高まる結果、定着性及び耐ブリーディング性についてはある程度向上させることができるものの、インクと共に色材も記録紙の奥深くまで浸透してしまうため、画像濃度や彩度が低下したりする等の不都合が発生する。その他、インクの横方向に対する広がりも発生する結果、画像のエッジのシャープさの低下や解像性の低下等の問題も同時に発生する。一方、後者の場合には、上記した前者に対する不都合に加え、記録ヘッドのノズル部での溶剤の蒸発による目詰まりが発生し易く好ましくない。

【0005】更に、上述した種々の問題点を改善する目的で、形成画像が良好となるような機能を有する液体組成物をインクの噴射に先だって記録媒体上に付着させておく方法が開示されている。例えば、特開昭63-299971号公報には、1分子当たり2個以上のカチオン性基を有する有機化合物が含有された液体組成物を、インクの噴射に先だって記録媒体上に付着させた後に、アニオン性染料が含有されたインクで記録する方法が記載されている。

【0006】又、特開昭63-60783号公報及び特開昭64-63185号公報には、塩基性ポリマーを含有する液体組成物を、インクの記録に先だって噴射する方法が開示されている。しかし、上記何れの方法もカチオン性基を有するポリマーを使用するため、染料の耐光性を著しく低下させてしまうという問題点があった。

【0007】一方、特開昭63-299970号公報及び特開平5-202328号公報には、記録媒体へのインクの付与に先だち、多価金属塩、即ち、種々の金属イオンとハロゲン化合物や有機酸等の陰イオンとの間でのイオン結合により形成された化合物を予め記録媒体上に付与しておき、その後インクで画像を形成する方法が開

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示されている。しかし、これら多価金属塩類は一般に、グリセリン、ジエチレングルコール等の有機溶剤への溶解性が低いため、液体組成物中に含有させてインクジェット記録を行う場合に用いると、液滴が噴出されるノズル先端で析出が生じ易く、ノズルの目詰まりの原因となってしまうという問題点があった。更に、インクに熱エネルギーを与えて気泡を発生させることにより液滴を吐出させて記録を行うインクジェット方式を利用する記録方法に、このような多価金属塩が含有された液体組成物を使用すると、発熱ヒーター上で上記多価金属が析出してしまい、液滴の吐出が停止してしまうという問題点もあった。

【0008】

【発明が解決しようとする課題】従って、本発明の目的は、上記実状に鑑み、下記6点の課題を解決した優れた画像形成方法に使用される液体組成物、及びこれを使用したインクセット、更にはこれらを用いた画像形成方法及び画像形成装置を提供することにある。即ち、普通紙に対するインクジェット記録を行った場合に、下記の記録特性を満足することを目的とする。

- (1) 良好な定着性を有しながら文字品位が良好であること。
- (2) 十分な画像濃度が得られ、ベタ画像の均一性が高いこと。
- 又、特に普通紙に対するカラー画像形成時において、下記の記録特性が満足されることを目的とする。
- (3) ブリーディングが防止されていること。
- (4) 色再現性が良好であり、高精細な記録画像が得られること。
- (5) 完全な耐水性を有する記録画像が得られること。
- (6) 記録画像が十分な耐光性を有していること。

【0009】

【課題を解決するための手段】上記目的は以下の本発明により達成される。即ち、本発明は、画像を形成するためのインクと共に使用する液体組成物であって、液体媒体中に金属配位化合物を含有させたことを特徴とする液体組成物、該液体組成物とインクとを組み合わせることを特徴とするインクセット、これらを用いる画像形成方法、及び上記液体組成物とインクセットを有する画像形成装置である。

【0010】本発明では、染料及び顔料等の色材を含まない液体組成物と、色材が含有されているインクとを記録紙上或いは記録紙に浸透した所で混合させて、インク中の色材を析出させることによって、本発明の目的を達成することができる。即ち、液体組成物中に含有されている金属配位化合物と、インク中に含有されている色材である少なくともアニオン性基を有する染料が、記録紙等の記録媒体上で混合される結果、金属配位化合物中の中心金属がインク中の色材と反応して色材が析出する現象が発生する。

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【0011】この現象は、配位子により取り囲まれて中心に配位されていた金属が、その中心から外れ、染料分子中のアニオン性基であるカルボキシル基やスルホン酸基等の酸性基と造塩（レーキ化）する現象である。一般に、水溶性染料と多価金属とが造塩されて作製されたレーキ染料が耐光性に優れていることはよく知られているが、本発明において析出するレーキ化物も従来知られているレーキ染料と同様に耐光性に優れている。又、本発明では、従来のレーキ染料をインクの色材として使用する際に必須であった分散工程も必要でなく、更にインク

【0012】更に、本発明において、レーキ化反応が速やかに進行する染料が使用されている場合には、画像の耐光性だけでなく、記録紙上での異なる色（記録ドット）間でのブリーディングの発生を防止することもできる。これは、前記したレーキ化反応時における染料の瞬時の析出によって、境界部でのインクの混合が防止されるためである。

【0013】一方、レーキ化反応の進行が遅い染料を使用する場合には、ブリーディングの発生を完全に防止することが困難な場合が生じる。本発明ではそのような場合に、液体組成物中に、前記金属配位化合物に加えて更に高分子化合物を含有させることによってブリーディングを有効に防止することができる。これは、配位子の中心金属のイオンの相互作用により中和され、析出しかかっている会合体が、該高分子化合物により吸着されて巨大な凝集体が生成する結果、境界部でのインクの混合が

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\*【0014】本発明によれば、上記したような染料の析出のため、染料化合物の多くが記録紙等の記録媒体の表面で定着する。このため、インクの定着性の向上のみならず、記録画像の発色性の向上、紙表面の繊維の影響による色ムラ、インクの裏抜け（紙の裏面へのインクの浸透）等の問題をも同時に解決することが可能となる。

【0015】

【発明の実施の形態】次に好ましい実施の形態を挙げて本発明を更に詳細に説明する。先ず、本発明の液体組成物について述べる。本発明の液体組成物を構成する成分としては、液媒体の他に（1）金属配位化合物、該金属配位化合物に加えて使用される（2）高分子化合物の2つが挙げられる。尚、この液体組成物には、染料及び顔料等の色材は含まれていない。以下、その夫々について述べる。

【0016】（1）金属配位化合物

金属配位化合物とは一般に、ある種の金属イオンが、該金属イオンに配位結合する能力を有する電子供与体（配位子）により取り囲まれた化合物のことである。このような金属イオンと配位結合可能な配位子を構成する元素としては、周期律表中の第5族及び第6族に属するものに限られ、N、O、P及びS等がその代表的な元素である。本発明においては特に、配位子中に窒素原子及び酸素原子が含まれている金属配位化合物を使用すると、染料のレーキ化反応が速やかに進行するため好ましい。これらの元素から構成される配位子の種類としては、1つの配位子（1分子）に電子供与基を1つ持つもの（1座配位子）と、2個以上の電子供与基を持つもの（多座配位子）に大別することができる。配位数毎に分類して配位子の具体例を下記表1に挙げる。

\* 【0017】表1：配位子の具体例

配位数	配位子種
1	アンモニア 水 酢酸 ハロゲン
2	グリシン エチレンジアミン プロピレンジアミン 乳酸
3	イミノジ酢酸 ジエチレントリアミン
4	ジヒドロキシエチルグリシン ヒドロキシエチルイミノジ酢酸 ニトリロ三酢酸
6	エチレンジアミン四酢酸 ヒドロキシエチルエチレンジアミン四酢酸
8	ジエチレントリアミン五酢酸
10	トリエチレンテトラミン六酢酸

本発明においては、これらの内、配位数2以上の配位子を有する金属配位化合物を好ましく用いることができる

が、より好ましくは、配位数3以上の配位子を有する金属配位化合物が好ましく用いられる。尚、本発明で使用

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することができる化合物は、表1に挙げた配位子を有するものに勿論限定されことなく、配位数が2以上の配位子を有する金属配位化合物であればいずれのものも好ましく使用することができる。

【0018】又、上記したような配位子によって配位される金属イオン（中心金属）としては、多価金属イオンであれば本発明においていずれも好ましく使用することが可能であるが、中でも、アルミニウムイオン、ニッケルイオン、銅イオン、バリウムイオン、カルシウムイオン、鉄イオン及びクロムイオン等が染料の耐光性を向上させる効果が大きく好ましい。本発明の液体組成物は、以上挙げたような配位子と金属イオンとにより構成される金属配位化合物が含有されていることを特徴とするが、該金属配位化合物の作製方法に関しては、無機化学の基礎（日本化学会編）等に記載の常法により行うことができる。又、本発明において液体組成物中に含有されるこれら金属配位化合物の量は、一般的には重量基準で0.05～8.0重量%が好適な範囲であるが、各々使用する物質の組み合わせにより、最適な範囲を決定する必要がある。

【0019】又、本発明の液体組成物においては、インクジェットヘッドの先端における目詰まり防止、及び熱エネルギーをインク及び液媒体に作用させて、これらの液体を噴射して記録を行なう際の吐出持続性向上等の目的から、液体組成物中における上記したような配位子に配位されていない状態の金属イオン濃度を減らすことが好ましい。このような配位子に配位されていない状態の金属イオン濃度を減らす方法としては、上記したような方法で金属配位化合物を作製する際に、十分に金属イオンと配位子との反応を行なわせる方法があり、該方法により配位されていない状態の金属イオンの発生を防止することができる。

【0020】特に、アルミニウムイオン、クロムイオン等の如く配位化合物の形成化反応が比較的遅いものは、反応時に煮沸等の操作をするのが好ましい。これによって配位されていない状態の金属イオン濃度を低減させることが可能となる。又、該反応の起こり易さは反応時の溶液pHにも影響されるため、金属及び配位子の組み合わせで最適なpHに調整して反応させるのがよい。

【0021】次に、上記した金属配位化合物に加えて本発明の液体組成物に含有させることができる（2）高分子化合物について説明する。前述の通り、本発明の液体組成物に添加する高分子化合物の役割は、記録媒体上でのインクのブリーディングを更に有効に防止することにある。従って、上記した金属配位化合物のみでもブリーディングの発生が見られない場合には添加する必要はない。しかし、レーキ化反応が遅い染料を使用する等の場合に、液体組成物中に数平均分子量が1,000以上の高分子化合物を更に含有させて用いるのが好ましい。数平均分子量が1,000以上の高分子化合物は、会合体

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を吸着し巨大な凝集体を形成し易いため、ブリーディングを有効に防止し得るためと思われる。

【0022】本発明の液体組成物に用いることができる高分子化合物としては、具体的には例えば、ポリアリアルアミン塩酸塩、ポリアミンスルホン塩酸塩、ポリビニルアミン塩酸塩、キトサン酢酸塩等のカチオン性ポリマー；アクリルアミド、ポリビニルアルコール、ポリビニルピロリドン等の非イオンポリマー等を挙げることができる。又、この他にも、非イオン性高分子物質の一部をカチオン化したカチオン性ポリマーであってもよい。具体的には、ビニルピロリドンとアミノアルキルアクリレート4級塩との共重合体、アクリルアミドとアミノメチルアクリルアミド4級塩との共重合体等を挙げることができるが、勿論本発明これらの高分子化合物に限定されないことは言うまでもない。

【0023】更に、上記した高分子物質及びカチオン性の高分子物質は水溶性であれば申し分ないが、ラテックスやエマルジョンのような分散体であっても構わない。本発明の液体組成物中に含有されるこれらの高分子化合物の量としては、0.05～20重量%が好適な範囲であるが、各々使用する他の物質の組み合わせにより、最適な範囲を決定する必要がある。

【0024】次に本発明の液体組成物を構成するその他の成分について具体的に述べる。本発明の液体組成物は、上記したような、（1）金属配位化合物、必要に応じて添加される（2）高分子化合物の他に、通常、水、水溶性有機溶剤等の液媒体及びその他の添加剤からなる。本発明で使用される水溶性有機溶剤としては、ジメチルホルムアミド、ジメチルアセトアミド等のアミド類；アセトン等のケトン類；テトラヒドロフラン、ジオキサン等のエーテル類；ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール類；エチレングリコール、プロピレングリコール、ブチレングリコール、トリエチレングリコール、1,2,6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール等のアルキレングリコール類；エチレングリコールメチルエーテル、ジエチレングリコールモノメチルエーテル、トリエチレングリコールモノメチルエーテル等の多価アルコールの低級アルキルエーテル類；エタノール、イソプロピルアルコール、n-ブチルアルコール、イソブチルアルコール等の1価アルコール類の他、グリセリン、N-メチル-2-ピロリドン、1,3-ジメチル-イミダゾリジノン、トリエタノールアミン、スルホラン、ジメチルサルホキサイド等が挙げられる。

【0025】上記水溶性有機溶剤の含有量については特に制限はないが、好ましくは5～60重量%、更に好ましくは5～70重量%の範囲とする。この他、本発明の液体組成物には、必要に応じて、粘度調整剤、pH調整剤、防腐剤、界面活性剤、酸化防止剤、蒸発促進剤等の

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添加剤を配合しても構わない。界面活性剤の選択は、液体の浸透性を調整するうえで特に重要である。本発明の液体組成物の物性として好適な範囲は、25℃付近でpHが3～12、表面張力が0～60 dyne/cm、及び粘度が1～30 cpsの各範囲である。

【0026】次に、本発明のインクセットを構成するインクについて説明する。本発明で使用するインクは、色材として少なくともアニオン性基を含有する水溶性染料を含有するものであればよく、その他の成分としては、通常のインクに用いられている水、或いは水と水溶性有機溶剤とからなる水性液媒体、及び必要に応じて添加される各種添加剤、例えば、粘度調整剤、pH調整剤、防腐剤、界面活性剤及び酸化防止剤等からなる。

【0027】本発明で使用するアニオン性基を含有する水溶性染料としては、カラーインデックス (COLOR INDEX) に記載されている水溶性の酸性染料、直接染料或いは反応性染料であれば特に制限はない。又、カラーインデックスに記載のないものでも、アニオン性基、例えば、スルホン基、カルボキシル基等を有するものであれば特に制限はない。ここで言う水溶性染料の中には、溶解度のpH依存性があるものも当然含まれる。中でも前述の金属配位化合物と染料との間におけるレーキ化反応の生じ易さという点では、染料分子中にカルボキシル基を有するものが好ましい。

【0028】本発明で使用する上記染料の具体例を以下に挙げる。イエローインクに使用される染料としては、例えば、C. I. ダイレクトイエロー142、144、86及びC. I. アシッドイエロー23等が挙げられ、マゼンタインクに使用される染料としては、例えば、C. I. アシッドレッド92、289、35、37、52等が挙げられ、シアンインクに使用される染料としては、例えば、C. I. アシッドブルー9、7、103、1、90、C. I. ダイレクトブルー86、87、199等が挙げられ、ブラックインクに使用される染料としては、例えば、C. I. フードブラック2、C. I. ダイレクトブラック52、154、195等が挙げられるが、本発明はこれらに限定されるものではない。

【0029】本発明で使用する上記染料の量はインク全体の0.1～10重量%が好ましい。使用量が0.1重量%より少ないと印字した文字等の判読が困難であり、使用量が10重量%より多いと染料によってはノズル目詰りの可能性が出てくるために好ましくない。

【0030】インクに使用される水溶性有機溶剤としては、前記した液体組成物に使用される水溶性有機溶剤を同様に使用することができる。これらの有機溶剤のインク中での含有量の好適な範囲についても同様である。又、インクの好適な物性範囲についても同様であり、25℃付近でpHが3～12、表面張力が0～60 dyne/cm、及び粘度が1～30 cpsの各範囲である。但し、表面張力については、液体組成物の表面張力をイ

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ンクの表面張力よりも低くした方が本発明の効果がより有効に発揮される場合があるために好ましい。この理由については、このような構成とすれば、印字プロセス上、例えば、先に打ち込まれる液体組成物が記録媒体上で後から打ち込まれるインクの濡れ性を均一にする効果があるためであろうと考えられるが、その詳細は明らかではない。

【0031】又、更に本発明の効果を一層向上させるために、インクに以上説明した成分の他に、アニオン性の界面活性剤若しくはアニオン性の高分子物質を添加してもよい。或いは、前記両性界面活性剤をその等電点以上のpHに調整して使用してもよい。アニオン性界面活性剤の例としては、カルボン酸塩型、硫酸エステル型、スルホン酸塩型、リン酸エステル型等、一般的なものを用いることができる。又、アニオン性高分子物質の例としては、アルカリ可溶型の樹脂、具体的には、ポリアクリル酸ソーダ或いは高分子の一部にアクリル酸を共重合したもの等を挙げることができるが、勿論本発明はこれらに限定されるものではない。

【0032】本発明の画像形成方法を実施する際に使用する記録媒体については特に制限されるものではなく、従来から使用されているコピー用紙、ボンド紙等のいわゆる普通紙が好適に使用される。勿論インクジェット記録用に特別に作製したコート紙やOHP用透明フィルムも好適に使用されるし、一般の上質紙や光沢紙も好適に使用可能である。

【0033】本発明の画像形成方法は、液体組成物を記録媒体の少なくとも画像形成領域に付着させる工程

(A)と、少なくともアニオン性化合物を含有するインクをインクジェット方式により前記記録媒体に付与する工程(B)とからなり、上記で述べた液体組成物とインクとを記録媒体の少なくとも画像形成領域と一緒に付着せしめて画像を形成する。尚、ここでいう画像形成領域には、画像形成領域の近傍も含まれる。ここで画像形成領域とは、インクのドットが付着する領域のことであり、画像形成領域の近傍とは、インクのドットが付着する領域の外側から1～5ドット程度離れた領域のことを指す。又、液体組成物とインクとを記録媒体の少なくとも画像形成領域に付着せしめる場合には、いずれを先に付着させても構わない。即ち、上記工程(A)を上記工程(B)に先だって行なってもよいし、工程(A)を工程(B)の後に行なってもよい。

【0034】液体組成物を記録媒体上に付着せしめる方法としては、スプレーやローラー等によって、記録媒体の全面に付着せしめる方法であっても勿論よい。しかし、インクが付着される画像形成領域及び画像形成領域の近傍のみに選択的且つ均一に液体組成物を付着させることができれば、より好ましい画像形成をすることができる。そのために本発明においては、液体組成物を記録媒体上に付着させる方法として、このような付着を行

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うことが可能なインクジェット方式を用いるのがより好ましい。又、インクジェット方式としては、いずれの方式のものでもよいが、特に、インクや液体組成物に熱エネルギーを付与することにより、これらの液滴をノズルより噴射させて記録を行なう方式のものは、高密度記録、高速記録及び高精細記録等を容易に実施するために特に好ましい。

【0035】又、インクの記録媒体上への付着は、インクジェット方式、より好ましくはオンデマンド型インクジェット方式によって行われるが、イエロー、マゼンタ、シアン、ブラック、レッド、ブルー及びグリーンの何れかの色のインクと、本発明の液体組成物とからなるインクセットを用い、上記のような熱エネルギーを作用させるインクジェット方式によりカラー記録を行えば、高速で、高密度且つ高精細なカラー画像を容易に形成することができる。この際、インクセットとして用いられる好ましいインクの色組合せとしては、イエロー、マゼンタ及びシアンの3色のセット、或いはこの3色にブラックを加えた4色のセットである。次いで、本発明の画像形成方法に用いられる記録装置について説明する。上記したように、本発明においては記録ヘッドのインクに記録信号を与え、発生した熱エネルギーにより液滴を吐出する方式が好ましい。その装置の主要部である記録ヘッドの構成を図1、図2及び図3に示す。

【0036】ヘッド13は、インクを通す溝14を有するガラス、セラミック、又はプラスチック板等と感熱記録に用いられる発熱抵抗体層を有する発熱ヘッド15

(図では薄型ヘッドが示されているが、これに限定されるものではない)とを接着して得られる。発熱ヘッド15は酸化シリコン等で形成される保護膜16、アルミニウム電極17-1及び17-2、ニクロム等で形成される発熱抵抗体層18、蓄熱層19、アルミナ等の放熱性の良い基板20より成っている。

【0037】インク21は吐出オリフィス22まで来ており、圧力Pによりメニスカス23を形成している。ここで、電極17-1及び17-2に電気信号が加わると、発熱ヘッド15のnで示される領域が急激に発熱し、ここに接しているインク21に気泡が発生し、その圧力でメニスカス23が突出し、吐出オリフィス22よりインク小滴24となり、記録媒体25に向かって飛翔する。図3には図1に示したノズルを多数並べた記録ヘッドの概略図を示す。該記録ヘッドは多数の流路を有するガラス板等27と図1において説明したものと同様の発熱ヘッド28を密着して作られる。尚、図1は、インク流路に沿ったヘッド13の断面図であり、図2は図1のA-B線での断面図である。

【0038】図4に、該ヘッドを組み込んだインクジェット記録装置の一例を示す。図4において、61はワイピング部材としてのブレードで、その一端はブレード保持部材によって保持されて固定端となり、カレンチレバ

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一の形態をなす。ブレード61は記録ヘッド65による記録領域に隣接した位置に配置され、又、本例の場合、記録ヘッド65の移動経路中に突出した形態で保持される。62は記録ヘッド65の吐出口面のキャップであり、ブレード61に隣接するホームポジションに配設され、記録ヘッド65の移動方向と垂直な方向に移動して、インク吐出口面と当接し、キャッピングを行う構成を備える。更に63はブレード61に隣接して設けられるインク吸収体であり、ブレード61と同様、記録ヘッド65の移動経路中に突出した形態で保持される。前記ブレード61、キャップ62及びインク吸収体63によって吐出回復部64が構成され、ブレード61、及びインク吸収体63によってインク吐出口面の水分、塵等の除去が行われる。

【0039】65は吐出エネルギー発生手段を有し、吐出口を配した吐出口面に対向する記録媒体にインクを吐出して記録を行う記録ヘッド、66は記録ヘッド65を搭載してその移動を行うためのキャリッジである。キャリッジ66はガイド軸67と摺動可能に係合し、キャリッジ66の一部はモーター68によって駆動されるベルト69と接続(図示せず)している。これによりキャリッジ66はガイド軸67に沿った移動が可能となり、記録ヘッド65による記録領域及びその隣接した領域の移動が可能となる。

【0040】51は記録媒体を挿入するための挿入部、52はモーター(図示せず)により駆動される紙送りローラーである。これらの構成によって記録ヘッド65の吐出口面と対向する位置へ記録媒体が給送され、記録が進行するにつれて、排出ローラー53を配した排出部へ排出される。上記構成において記録ヘッド65が記録終了等でホームポジションに戻る際、吐出回復部64のキャップ62は記録ヘッド65の移動経路から退避しているが、ブレード61は移動経路中に突出している。この結果、記録ヘッド65の吐出口面がワイピングされる。尚、キャップ62が記録ヘッド65の吐出口面に当接してキャッピングを行う場合、キャップ62は記録ヘッドの移動経路中に突出するように移動する。

【0041】記録ヘッド65がホームポジションから記録開始位置へ移動する場合、キャップ62及びブレード61は前記したワイピング時の位置と同一の位置にある。この結果、この移動においても記録ヘッド65の吐出口面はワイピングされる。前記の記録ヘッド65のホームポジションへの移動は、記録終了時や吐出回復時ばかりではなく、記録ヘッド65が記録のために記録領域を移動する間に所定の間隔で記録領域に隣接したホームポジションへ移動し、この移動に伴って上記ワイピングが行われる。

【0042】図5は、ヘッドにインク供給部材、例えば、チューブを介して供給されるインクを収容したインクカートリッジ45の一例を示す図である。ここで40

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は供給用インクを収容したインク収容部、例えば、インク袋であり、その先端にはゴム製の栓42が設けられている。この栓42に針（図示せず）を挿入することにより、インク袋40中のインクをヘッドに供給可能ならしめる。44は廃インクを受容するインク吸収体である。インク収容部としては、インクとの接液面がポリオレフィン、特にポリエチレンで形成されているものが好ましい。本発明で使用するインクジェット記録装置としては、前記の如きヘッドとインクカートリッジが別体となったものに限らず、図6に示す如きそれらが一体となったものも好適に用いられる。

【0043】図6において、70は記録ユニットであって、この中にインクを収容したインク収容部、例えば、インク吸収体が収納されており、かかるインク吸収体中のインクが複数のオリフィスを有するヘッド部71からインク滴として吐出される構成になっている。インク吸収体の材料としては、例えば、ポリウレタンを用いることができる。72は記録ユニット内部を大気に連通させるための大気連通口である。この記録ユニット70は、図4で示す記録ヘッドに代えて用いられるものであって、キャリッジ66に対し着脱自在になっている。尚、本発明に使用する記録装置において、上記ではインクに熱エネルギーを作用させてインク液滴を吐出するインクジェット記録装置を例に挙げたが、そのほか圧電素子を使用するピエゾ方式のインクジェット記録装置でも同様に利用することができる。

【0044】さて、本発明の記録方法を実施する場合に \*

#### M-1の成分

・金属配位化合物（アルミニウム-エチレンジアミン四酢酸配位化合物）

1. 0部

・アクリルアミドポリマー

0. 5部

・チオジグリコール

15. 0部

・水

残部

【0048】次に下記の成分を混合し、更にポアサイズが0. 22 $\mu$ mのメンブレンフィルター（商品名；フロポアフィルター、住友電工製）にて加圧濾過してイエ

#### イエローのインク（1）-Yの組成

・C. I. ダイレクトイエロー142

3部

・チオジグリコール

12部

・アセチレノールEH（川研ファインケミカル製）

0. 05部

・水

残部

#### 【0049】マゼンタのインク（1）-Mの組成

染料を3部のC. I. ダイレクトイエロー142から、3. 5部のC. I. アシッドレッド92に代えた以外は（1）-Yと同じ組成。

#### シアンのインク（1）-Cの組成

染料を3部のC. I. ダイレクトイエロー142から、2. 7部のC. I. アシッドブルー9に代えた以外は（1）-Yと同じ組成。

#### ブラックのインク（1）-Kの組成

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\*は、例えば、前記図3に示した記録ヘッドをキャリッジ80上に5個を並べた記録装置を使用する。図7はその一例である。81、82、83及び84はそれぞれイエロー、マゼンタ、シアン及びブラック各色のインクを吐出するための記録ヘッドである。又、85は液体組成物を吐出するヘッドである。これらのヘッドは前記した記録装置に配置され、記録信号に応じて各色のインク及び液体組成物を吐出する。図7では記録ヘッド5個を使用した例を示したが、これに限定されるものではなく、図8に示したように、1本の長尺記録ヘッドでイエローインク、マゼンタインク、シアンインク、ブラックインク及び液体組成物を液流路を分けて吐出するのも好ましい。

【0045】

【実施例】以下に実施例を挙げて更に本発明を具体的に説明する。尚、文中「部」又は「%」とあるのは、特に断りのない限り全て重量基準である。

#### 【0046】実施例1

まず、下記の成分を混合溶解した後、ポアサイズが0. 22 $\mu$ mのメンブレンフィルター（商品名；フロポアフィルター、住友電工製）にて加圧濾過し、更に逆浸透法により液中の配位していない金属イオンを取り除き、無色の液体組成物M-1を得た。この時のpHは4. 0に調整した。尚、液体組成物及びインクにおける水の量は、構成成分の総和が100部となるように調整した。

【0047】

※ロー、マゼンタ、シアン及びブラックの各インク（1）-Y、（1）-M、（1）-C及び（1）-Kを得た。

染料をC. I. ダイレクトイエロー142から、C.

I. フードブラック2に代えた以外は（1）-Yと同じ組成。

【0050】次に、上記のようにして得られた液体組成物及び各色のインクを用いて、市販のコピー用紙及びボンド紙に記録を行った。使用したインクジェット記録装置としては、図4に示したものと同様の記録装置を用い、図7に示した5個の記録ヘッドを用いてカラー画像を形成した。尚、ここで用いた記録ヘッドは、360d

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p i の記録密度を有し、駆動条件としては駆動周波数を5 kHzとし、又、1ドット当たりの吐出体積は40 p lであった。これらの記録条件は本発明の実施例を通じて統一してある。又、印字テストの際の環境条件は、25℃/55%RHに統一してある。

【0051】記録画像の評価は次の方法で行った。

#### 1. 画像濃度

ベタ画像を液体組成物とブラックインクで形成し、12時間放置後の反射濃度を反射濃度計マクベスRD915（マクベス社製）にて測定した。評価基準は以下の通りである。

○：反射濃度が1.25以上

△：反射濃度が1.15～1.24

×：反射濃度が1.14以下

#### 【0052】2. 文字品位

液体組成物とブラックインクを用いて、ブラックの英数文字を記録し目視にて評価した。フェザリングが目立たないものを○として、それ以下のレベルのものについては×とした。

#### 【0053】3. ブリーディング

液体組成物とイエロー、マゼンダ、シアン及びブラックの各色のインクを用いて、ベタ部を隣接して記録し、各色の境界部でのブリーディングの程度を目視により観察した。ブリーディングが実質上問題ないレベルにあるものを○とし、それ以下のレベルのものは×とした。

#### 4. 画像耐光性

上記1、2及び3の評価試験で得られた記録画像にキセノン光を50時間照射し、照射前後での反射濃度（OD値）の残存率（%）を測定した。OD残存率が90%以上のものを○とし、それ以下のものは×とした。

#### 【0054】5. 連続吐出性

液体組成物を図7に示した記録ヘッドを使用して、100,000,000回の連続パルスを与え吐出持続性を評価した。試験終了時まで継続的に吐出が行なえたものを○とし、試験途中で吐出が停止したものを×とした。試験に使用したノズル数は1ヘッド当たり3ノズルとした。尚、本発明の実施例においては、液体組成物の記録

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媒体への付着領域は、インクの画像形成領域と同一領域であり、記録媒体にインクが打ち込まれている部分には、1：1で対応して液体組成物が打ち込まれている。更に、印字方向は片方向であり常に液体組成物がインクよりも先に打ち込まれている。

#### 【0055】比較例1

実施例1で使用した液体組成物を使用しなかったことを除いては、実施例1と全く同様にして記録及び評価試験を行った。実施例1及び比較例1の評価試験の結果をまとめて表2に記載する。表2から明らかなように、実施例1では画像濃度、文字品位、ブリーディング及び耐光性の各評価について何れも良好な結果が得られたのに対し、比較例1では、低濃度な画像しか得られず、ブリーディングが発生し、しかも画像の耐光性にも劣っていた。

【0056】表2：実施例1及び比較例1の評価結果

評価項目	実施例1	比較例1
画像濃度	○	×
文字品位	○	○
ブリーディング	○	×
画像耐光性	○	×
連続吐出性	○	×

#### 【0057】実施例2～6

次に、表3に記載した成分を使用して、表4に示した成分で構成される液体組成物とインクを作製し、実施例1と全く同様にして、実施例2～6の記録及び評価試験を行った。但し、表4に記載されている成分以外の成分については、実施例1と同じ成分が含まれている。この結果、実施例2～6についても、表2に記載した実施例1の場合と同様に、画像濃度、文字品位、ブリーディング及び耐光性の各評価について何れも良好な結果が得られた。

【0058】表3：本発明の実施例2～6に使用した金属配位化合物

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番号	金属配位化合物	製造方法	構造
1	ニッケル-ヒドロキシエチレンジアミン四酢酸配位化合物	HEDTA (商品名、キレスト(株)製) とニッケルを等量(1モル:1モル) 混合したもの	$  \begin{array}{c}  \text{HOCH}_2\text{CH}_2 \quad \text{CH}_2\text{COOH} \\  \diagdown \quad \diagup \\  \text{NCH}_2\text{CH}_2\text{N} \\  \diagup \quad \diagdown \\  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH}  \end{array}  + \text{Ni}  $ <p style="text-align: center;">HEDTA</p>
2	銅-ニトリロ三酢酸配位化合物	NTA (商品名、キレスト(株)製) と銅を等量(1モル:1モル)混合したもの	$  \begin{array}{c}  \text{CH}_2\text{COOH} \\  \diagdown \\  \text{N} \\  \diagup \\  \text{CH}_2\text{COOH} \\  \diagdown \\  \text{CH}_2\text{COOH}  \end{array}  + \text{Cu}  $ <p style="text-align: center;">NTA</p>
3	バリウム-ジェチレントリアミン五酢酸配位化合物	TTHA (商品名、キレスト(株)製) とバリウムを等量(1モル:1モル) 混合したもの	$  \begin{array}{c}  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \\  \diagdown \quad \diagup \\  \text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N} \\  \diagup \quad \diagdown \quad \diagup \quad \diagdown \\  \text{HOOCCH}_2 \quad \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH} \quad \text{CH}_2\text{COOH}  \end{array}  + \text{Ba}  $ <p style="text-align: center;">TTHA</p>
4	アルミニウム-ヒドロキシエチレンジアミン四酢酸配位化合物	HEDTA (商品名、キレスト(株)製) とアルミニウムを等量(1モル:1モル) 混合したもの	$  \begin{array}{c}  \text{HOCH}_2\text{CH}_2 \quad \text{CH}_2\text{COOH} \\  \diagdown \quad \diagup \\  \text{NCH}_2\text{CH}_2\text{N} \\  \diagup \quad \diagdown \\  \text{HOOCCH}_2 \quad \text{CH}_2\text{COOH}  \end{array}  + \text{Al}  $ <p style="text-align: center;">HEDTA</p>

【0059】表4：実施例2～6の液体組成物の組成表

実施例	金属配位化合物	金属配位化合物含有量 (wt%)	その他の組成	液体組成物の pH
2	No.1	2.0	実施例1と同じ	6.0
3	No.2	1.5	実施例1と同じ	5.0
4	No.3	0.5	実施例1と同じ	8.0
5	No.4	1.2	実施例1と同じ	3.8
6	No.1	1.8	実施例1と同じ	6.0

## 【0060】

【発明の効果】以上説明したように、本発明によれば、普通紙に対するカラーインクジェット記録を行う場合に、画像濃度及び文字品位が高く、ブリーディングが発生せず、良好な耐光性を満足した画像を得ることができる。尚、本発明の液体組成物は連続吐出性にも優れている。

## 【図面の簡単な説明】

【図1】インクジェット記録装置のヘッド部の縦断面図である。

【図2】インクジェット記録装置のヘッド部の横断面図である。

【図3】インクジェット記録装置のヘッド部の外観斜視図である。

【図4】インクジェット記録装置の一例を示す斜視図である。

【図5】インクカートリッジの縦断面図である。

【図6】記録ユニットの斜視図である。

【図7】本発明の実施例で使用した複数の記録ヘッドが配列した記録部を示した斜視図である。

【図8】本発明に使用する別の記録ヘッドの斜視図である。

## 【符号の説明】

13：ヘッド

14：インク溝

15、28：発熱ヘッド

16：保護膜

17：アルミニウム電極

18：発熱抵抗体層

19：蓄熱層

20：基板

21：インク

22：吐出オリフィス（微細孔）

23：メニスカス

24：インク小滴

25：記録媒体

26：マルチ溝

27：ガラス板

40：インク袋

42：ゴム製の栓

44：インク吸収体

45：インクカートリッジ

51：給紙部

52：紙送りローラー

52：排紙ローラー

61：ブレード

62：キャップ

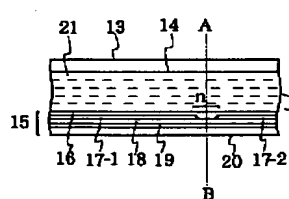
63：インク吸収体

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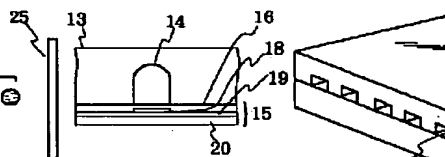
64 : 吐出回復部  
 65 : 記録ヘッド  
 66 : キャリッジ  
 67 : ガイド軸  
 68 : モーター  
 69 : ベルト  
 70 : 記録ユニット  
 71 : ヘッド部

72 : 大気連通口  
 80 : キャリッジ  
 81 : イエローのインクを吐出するための記録ヘッド  
 82 : マゼンタのインクを吐出するための記録ヘッド  
 83 : シアンのインクを吐出するための記録ヘッド  
 84 : ブラックのインクを吐出するための記録ヘッド  
 85 : 液体組成物を吐出するための記録ヘッド

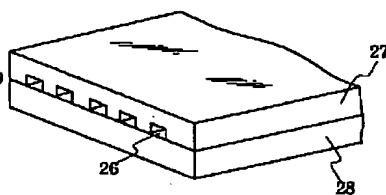
【図1】



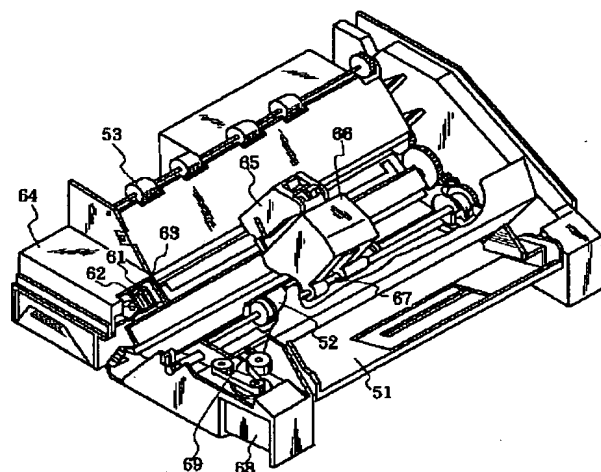
【図2】



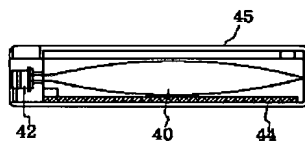
【図3】



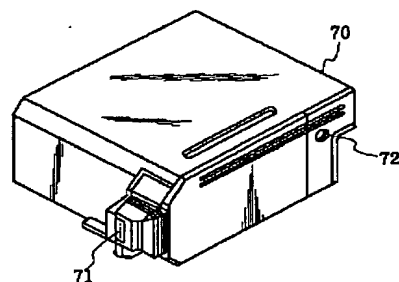
【図4】



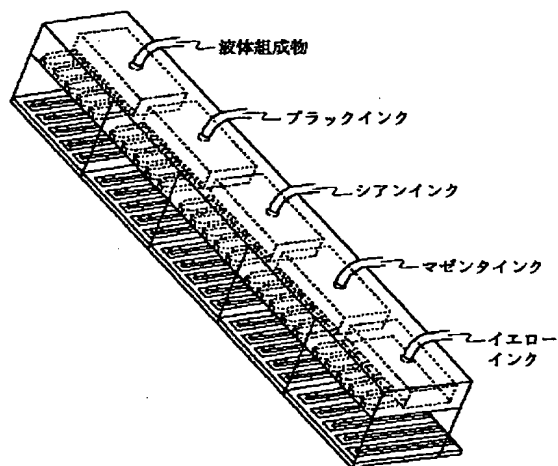
【図5】



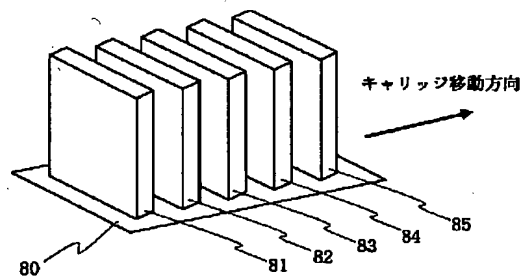
【図6】



【図8】



【図7】



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フロントページの続き

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